

**Preservation of Rock Samples: Geochemical Investigation
and Implication on Source Rock Assessment**

BY

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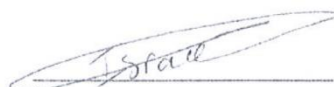
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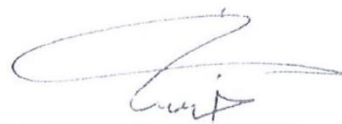
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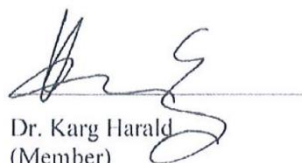
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“Research is to see what everybody else has seen, and to think what nobody else has thought.”

– Albert Szent-Gyorgyi. First and foremost, I would like to praise and thank **God**, the Almighty, who has granted countless blessings, and knowledge.

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Abbreviations

CO ₂	Carbon dioxide	GC-MS	Gas chromatography mass selective
H ₂ S	Hydrogen sulfide	CO	Carbon monoxide
SRA	Source rock analyzer	SO ₂	Sulfur dioxide
TOC	Total organic content	C ₃	Ethane
T _{MAX}	Maximum temperature	C ₄	Butane
S1	Free hydrocarbons present in the sample	C ₇	Heptane
S2	Volume of hydrocarbons that formed during thermal pyrolysis of the sample	C ₁₅	Pentadecane
S3	CO ₂ yield during thermal breakdown of kerogen	C ₁₁	Undecane
S4	Residual carbon content of the sample	C ₁₂	Dodecane
OSI	Oil saturation index	UV	Ultraviolet
PI	Productivity index	IR	Infrared
HI	Hydrogen index	MN	Month
OI	Oxygen index	PVT	Pressure volume temperature
FID	Flame ionization detector	S	Sulfur
S _o	Oil saturation	W	Week

TD	Thermal desorption	UP	Un preserved
T	Temperature	API	The American petroleum institute
°C	Celsius	h	Hour
°F	Fahrenheit	bbls/acft	Barrel per acre-foot
R _o	Vitrinite reflectance	C1	Core 1
wt%	Weight percentage	C2	Core 2
psig	Pounds per square gauge	C3	Core 3

Abstract

Full Name: Ali Hussain Al Eid
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The primary importance of the preservation of cores collected during drilling is to maintain the core and its fluids as close as possible to in-situ conditions. Fluid loss resulting from poor preservation (evaporation and expulsion) is a major problem in sampling source and reservoir rocks for laboratory analysis. Free hydrocarbons in the rock sample are greatly affected by the sample preservation conditions. Pyrolysis parameters are affected by the preservation process and its duration due to the mass loss of hydrocarbons over long storage times and poor preservation. This research project aims to determine the impact of extensive sample storage time and delayed sample processing and analysis on the results obtained from geochemical analyses. A specific experimental design and sample selection strategy has been followed to achieve optimal results towards an enhanced uncertainty estimate when dealing with geochemical data from samples that have been exposed to variable storage times. Well-preserved core samples were used to conduct this study. Each preserved core was run individually for pyrolysis through consistent time cycles. Results from each run were plotted to determine the effects of sample storage time and analytical delays after sample extraction from the well. Furthermore, existing pyrolysis measurements from the non-preserved core from the same wells were compared with the results obtained from the

preserved samples. Overall, results from preserved samples show no significant changes in pyrolysis parameters. However, comparisons between pyrolysis results from preserved and un-preserved core samples from the same interval show significant drops in free hydrocarbon (S1), potential hydrocarbon (S2) and total organic content (TOC) measurements for un-preserved samples. Those changes are interpreted as results of hydrocarbon losses due to poor sample preservation prior to lab analysis. In conclusion, relying on unrepresentative pyrolysis measurements from poorly preserved samples can critically impact results used for many geochemical applications and source rock assessment.

ملخص الرسالة

الاسم الكامل: علي حسين ال عيد

عنوان الرسالة: حفظ عينات الصخور: الاستقصاء الجيوكيميائي والتأثير على تقييم صخر المصدر

التخصص: جيولوجيا

تاريخ الدرجة العلمية: مايو , 2023

إن الحفاظ على عينة الصخر الذي تم جمعها أثناء الحفر يعتبر ذو أهمية أساسية للحفاظ على سوائل العينة قدر الإمكان. يعتبر تبخر وفقدان السوائل الناتجة عن سوء الحفظ مشكلتين رئيسيتين عند اخذ العينات للتحليل المختبري. تتأثر الهيدروكربونات الحرة في عينة الصخور بشكل كبير بظروف حفظ العينة وبالتالي تتأثر معلمات الانحلال الحراري بعملية الحفظ ومدته بسبب فقدان كتلة الهيدروكربون مع مرور الوقت. يهدف هذا البحث إلى تحديد تأثير وقت تخزين وتأخر تجهيز العينات وتحليلها على النتائج الجيوكيميائية التي يتم الحصول عليها. تم إجراء تصميم تجريبي واستراتيجية محددة لاختيار العينات لتحقيق النتائج المثلى. أثناء هذه الدراسة, تم اختيار عينات محفوظة جيداً. واختبار كل عينة بشكل فردي للتحلل الحراري من خلال دورات زمنية متسقة. بعدها, تم رسم النتائج من كل اختبار زمني لتحديد آثار وقت تخزين العينة والتأخيرات التحليلية بعد استخراج العينة من البئر. علاوة على ذلك، تمت مقارنة نتائج العينات المحفوظة جيداً مع عينات غير محفوظة من نفس الآبار المعنية. بشكل عام، النتائج من العينات المحفوظة تظهر عدم وجود تغييرات ملموسة في معاملات الانحلال الحراري مع تقلبات ضئيلة. لكن، تُظهر المقارنات بين نتائج الانحلال الحراري من العينات المحفوظة وغير المحفوظة من نفس الطبقة انخفاضاً كبيراً في قياسات الهيدروكربون المتمثلة في معاملات الانحلال الحراري. يرجح تفسير هذه التغييرات على أن نتائج خسائر الهيدروكربون كانت بسبب سوء حفظ العينات قبل التحليل المعمل. ختاماً, الاعتماد على قياسات الانحلال الحراري من العينات المحفوظة او المحفوظة بشكل غير جيد يمكن أن تؤثر بشكل حاسم على نتائج العديد من التطبيقات الجيوكيميائية لتقييم صخور المصدر.

Chapter 1

Introduction

1.1 Background

Geoscientists utilize numerous technologies and approaches to predict oil and natural gas occurrences in the subsurface. Subsurface rock samples offer valuable geological information as they provide material that can be studied for many physical and chemical properties and used as calibration parameters for geological models. Thus, the implications of the accuracy and reliability of these data can be significant.

Through rock geochemistry, exploration efficiency can be enhanced by accounting for many of the variables that control the volumes of crude oil and natural gas, including source-rock distribution, organic richness, and thermal maturity (Al Eid et al. 2020; Abu-Mahfouz et al. 2019, 2022, 2023; Peters, 2022; Karg et al. 2022; Grohmann et al. 2023). However, serious issues during core transport, preservation and storage can cast uncertainty on the results of such studies. Thus, ensuring good quality of cores is critical. Core handling on surface, transport, and storage times need to be minimized to ensure accurate reconstruction of original reservoir conditions. This challenge was tackled by multiple studies to find out the possible reasons for the loss of light hydrocarbon (e.g., Bajsarowicz; 1992, Auman et al. 1989; Torsaeter et al. 1985; Suliman et al. 2008; Collee et al. 1994; Skopec et al. 1995; Michael et al. 2013; Jiang et al. 2015; Zeng et al. 2021; Noble et al. 1997; Michael et al. 2014; and Bhosle et al. 2015).

Extensive holding of rock samples, preservation, and storage times have considerable effects on lab analysis results (Bhosle et al. 2015). Evaporation and migration of fluids (fluid loss) resulting from poor preservation are thought to be two key problems in sampling source and reservoir rocks for laboratory analysis (Ubani, 2013). Hydrocarbon evaporation and loss caused by inappropriate sample preservation are challenging, particularly for the estimation of oil and gas in-place volumes (Li et al. 2022). Therefore, several essential steps need to be taken to uphold an excellent preservation environment over an extended period.

There are many important steps to be considered to maintain an optimal preservation environment over a long storage period prior to lab analysis. Several core preservation techniques have been used in the oil and gas industry including quick freezing, wrapping cores with plastic wrap and aluminum foil followed by wax coating, placing the core in plastic sacks that can be sealed, and sealing the core samples in plastic or metal tubes (Basan et al. 1988; Hunt & Cobb, 1988; Basu et al. 2020; Li et al. 2022). Current industry technics use more efficient preservation methods to prevent breakage during handling & storage and most importantly preserve core fluids to ensure precise analyses.

Identifying the impact of long-term rock sample storage and preservation on source rock geochemical results can help to constrain a data correction model, reduce uncertainty, and suggest an ideal workflow for better future coring and preservation plans. Considering all these challenges and to end up with more representative results, there is an industry-wide need to revise sample storage, processing, and analysis time to avoid these issues and control light hydrocarbon losses.

1.2 Statement of the Problem and Research Objectives

Reservoir rock undergoes changes during the coring process, retrieval and on-site preparation before arriving at the laboratory. Sample preparation time and preservation methods during conventional coring activities impact geochemistry analysis results) Al Eid et al. 2020). The accuracy of the rock properties measured from subsurface samples can be affected by several factors such as sample contamination, fluid contamination, sample handling and preparation, sample evaporation, and sample storage conditions. Core alteration, losses of water content or light hydrocarbons can be mitigated by understanding the processes that affect the sample preservation (Bajsarowicz, 1992). Representative rock materials are to be obtained with the least physical alteration of the rock during drilling, handling and storage.

Data accuracy has significant implications, especially in equity determinations. Laboratory tests demonstrate that exposure of core to atmospheric conditions once extracted from the subsurface for even a short period of 30 min can result in up to 25% loss in water (American Petroleum Institute, 1960).

Losses of light hydrocarbons are a well-known problem in geochemical data analysis. Reported changes in the amount of free hydrocarbons over time have consequences in many aspects such as determining the sweet spots by identifying the oil-saturated intervals and calculating oil-in-place volumes.

This research project aims to determine the potential impact of extensive sample storage time and delayed sample processing and analysis on the results obtained from geochemical analyses. More specifically, the study attempts to determine any

significant differences in the results that can be obtained from basic source-rock geochemical screening analyses after different storage times, highlighting the main factors that control the analytical results. The study also aims to examine how good and poor preservation affects these results.

The main research questions that are addressed by this study are listed as follows:

- What is the impact of long-term core preservation on source rock geochemical results (S1, S2, TOC, and T_{MAX})?
- Are there any significant differences in the results that can be obtained from basic source-rock geochemical screening analyses after different storage times and preservation conditions (good or bad)?
- What are the main factors that enhance the preservation of source rocks and mitigate sample deterioration?
- What are the implications and recommendations for future source rock data assessment from core material?

Chapter 2

Literature Review

2.1 Methods of Core Preservation

The methods of preservation and packing of the core vary depending on the type of core and the core analysis measurement required. In the past, common industry practice has involved the placement of gypsum between the rock formation core material and the coring tool inner barrel in protecting and avoiding core damage during transport and handling. This method was not sufficient to achieve full preservation, particularly of the core's fluids from atmospheric pressure and chemical changes. Therefore, additional steps were implemented during the last decades to keep the samples preserved and in the most representative conditions to the subsurface (Basu et al. 2020; Li et al. 2022).

One of the challenges for handling and preserving source rocks for characterization is the selection of non-reactive sealing preservation material that prevents fluid loss or the adsorption of contaminants.

Two methods are commonly used for core preservation; either dry or wet. Preventing fluids evaporation can be considered a dry method, while wet methods of preservation involve submerging the core in brine or other fluid that preserves core wettability (Basan et al., 1988). For example, one of the dry core preservation methods is sealing in metal cans which acts as a vapor barrier. However, these metal cans react with the core and fluids causing changes in the core origin (Bajsarowicz, 1992).

Other methods are rubber, plastic, aluminum sleeves, fiberglass liners, and pressure steel core barrels to cover the core. This preservation technique is not suitable for keeping the evaporites for a long time (Bajsarowicz, 1992).

Wrapping the core in heat-sealed plastic bags was also used as a protection technique. Plastic shows some limitations as it is not an absolute oxygen vapor barrier due to its porous nature. It is sufficient only to minimize the rate of evaporation. Cores in this type of preservation lost up to 6% of their water content in only 10 days (Auman, 1989). During his study, Auman (1989) showed the time core samples need to lose their water content (i.e. water evaporation). One core plug was wrapped in plastic only and three others were sealed in heat-sealed plastic bags. Of these three, one was cut with scissors, one was punctured, and one was left intact. The results were plotted between the water retention qualities of various materials as water loss (grams) and time (in days) and demonstrated that the sample preserved only using plastic wrap lost 30% of its water content in 3 days. The preserved samples showed progressively less water loss with smaller hole sizes in the plastic wrap.

To minimize the loss of the volatile hydrocarbons in unconsolidated cores, freezing cores in dry ice is one of the most common techniques (Torsaeter, 1985). This freezing technique, however, has two challenges: (1) the light hydrocarbon fraction is not maintained at dry ice temperatures and (2) a variety of studies examining the implications of freezing on porosity and permeability showed inconsistent results (e.g., Torsaeter, 1985). The freezing process may affect the rock structure due to ice

formation (expansion) and the wettability due to the precipitation of hydrocarbons onto pore surfaces.

To test the efficiency of the nitrogen freezing technique and to improve its sealing quality, a study by Suliman (2008) was done to prove the superiority of using polyurethane foam injection over the nitrogen freezing technique. Results showed that core samples preserved with polyurethane foam injection revealed higher core stability over a longer period of time than did the ones preserved with the nitrogen freezing technique.

Recently, a high-viscosity gel is considered a new technology that was also used for downhole preservation purposes as an alternative to wellsite core preservation (Collee et al., 1994). For this method, a high molecular weight polypropylene glycol, non-soluble in water and environmentally friendly, is used. Laboratory tests indicate no spurt loss and zero water loss at 200F and 250 psig on water-saturated gel-coated rocks with permeabilities as high as 10 Darcy. Adding to this, this preservation gel is compatible with most water- and oil-based drilling fluids. It comes in direct contact with the core during and immediately after it is cut with minimized exposure to drilling fluid. This technique was used in obtaining in-situ measurements of remaining oil saturation (S_o) in two sandstone formations in the North Sea (Skopec, 1995). The core was cut with oil-based mud. Results showed that gel can provide an added measure of protection against core damage in highly permeable rocks. The relative permeability and reservoir modeling can benefit from gel-core residual oil measurements.

Among the different preservation techniques, coating cores with hot high-quality wax specifically designed for core sample preservation is an extensively used preservation

technique in many oil and gas operations. This method includes wrapping the core in plastic wrap and aluminum foil and then dipping the core in paraffin or a plastic sealant. This type of wax is very high impermeability with a flash-point exceeding 285°C (550°F) while recommended application temperature is between 160°C and 165°C (320°F and 330°F) (Bajsarowicz, 1992).

During this method, cores are enfolded in multiple layers of plastic wrap or film to prevent fluids in the core from contacting the outer wrapping of aluminum foil. To evaluate the efficiency of different wrapping materials, Hunt and Cobb (1988) compared two popular food wraps (Barex® and the food Saran® wrap) for different hydrocarbon fluids through their weight loss after 30 days of exposure at 100°F. Results showed that Barex® has achieved better results with less weight loss at the same condition than the Saran wrap. They found that Saran Wrap® is the least reactive with formation fluids. However, the wrap has been found to degrade with some hydrocarbon compositions, and does not serve as a barrier to oxygen or water vapor. On the other hand, Barex® film is inert against organic solvents and corrosive fluids. However, it is inflexible and difficult to wrap around the core.

2.2 Wellsite Core Handling & Preservation

At the well site, specific pull-out and lay-down core procedures are performed to prevent bending and fracturing. A hydraulic shear clamp is usually used to prevent core damage while breaking connections. It cuts the tube and insulates the core from the relative rotation of the two inner tubes, and keeps the core in the tube during lay-down. This is followed by a slow and careful laying down process against bending and impact damage. In some conditions, well-site core preservation involves the placement of gypsum between the core material and the coring tool inner barrel to stabilize and protect the core and to prevent core damage during transport, handling, slabbing and plugging.

Moreover, to preserve the core sample with its evaporation and fluids, wax dipping is usually suggested. This extra process is known as one of the most effective methods to prevent physical alteration of core samples throughout time as well as to maintain original core fluids and their distribution inside the core as they were when cut in formation. Wax preservation requires melting wax at medium temperatures using a range of melting tanks that has been designed for heating materials such as oil, water, vinyl compounds and waxes. Wax melters are used in a wide variety of industries and are suitable for the melting of the wax. Normally, wax melters have capacities from 0.7 kg to 1000 kg or greater and they can be built to the customer's specific requirements with a temperature range of up to 300°C. At the drilling sites, wax is usually prepared 30 mins before dip coating samples. After the core is cut into core samples (usually 1-foot lengths) and properly labeled with a marker, samples get out from the tube to be enfolded in plastic wrap (2-3 layers) to ensure that the core is isolated from any wax

contact. This wrapping is followed by enfolding the sample in aluminum foil with two layers. After that, a handle is made from soft wire by using universal pliers and cutter pliers such as identification marks facing upwards.

After that, samples are submerged into the melted wax to be coated, a process performed for a couple of seconds. Samples then are hung above the wax rack and wait for the filaments to cool down and the first coat of wax can harden. A second dip is usually performed to create a thick protected layer. After labeling the samples, a third layer of wax coating is generated to seal the label. Finally, the wires are removed before the sample is cooled down. A fourth and final coating is applied to the sample to cover the wire track for a perfect seal.

2.3 Storage & Processing Delay

A study done by Jiang (2015) argued that conducting laboratory analyses immediately after conventional coring can detect light oil components in shale cores. Furthermore, results from Thermal-Desorber Gas Chromatograph Mass Spectrometer Flame Ionization Detectors (TD-GC-MS/FID) showed that light hydrocarbons, including propane and butane, can exist in shale cores even after 6 months of storage at ambient conditions (Michael et al., 2013; Jiang, 2015). Through this study, the consequence of evaporative loss on the light hydrocarbons was proved by a comparison between a freshly prepared sample and the same powdered shale sample after being either stored in a sealed container or exposed to air without preservation. The freshly ground shale

sample was enriched in C₃ to C₄-hydrocarbons. However, the C₃ to C₇ hydrocarbons were absent from the same sample just after a week of storage in a capped sealed vial.

A recent study by Zeng (2021) has demonstrated the hydrocarbon losses by comparing light hydrocarbon losses of crude oils and pyrolysis yields under ambient conditions. Zeng worked to find out the possible controlling factors of light hydrocarbon loss. In his study, five shale cores with a total organic content of up to 3.5 wt% from different maturity levels (different vitrine reflectance R_o) were stored using liquid nitrogen freezing at -196°C. In addition, five crude oil samples of different API gravity (33-51°) were produced from the same formation for a fair comparison. Core samples were analyzed immediately after bringing them to the surface and others were exposed to ambient conditions for different time periods. Results showed a clear relationship between the total weight losses and thermal maturity/oil API gravity of samples. The total weight losses have increased with the increase of shale maturity level and oil API gravity. Compared with crude oils, 70% of weight losses in the rock were recorded within S1, whereas the crude oils were overall less in weight by 30%. Unlike crude oil, more light hydrocarbons are contained and kept within the rock.

Noble et al. (1997) conducted a series of evaporation experiments on crude oil samples of different API gravity. Noble et al. (1997) concluded that the determined weight loss increases with increasing API gravity. A relationship between the light aromatic fraction (C₁₅-) of lost hydrocarbons and oil API gravity was established and used to estimate shale oil volumes by Michael et al. (2014). Michael et al. (2014) attempted to correct the mass of light oil lost due to evaporation during core recovery. The findings

stated that the oil lost during core recovery is mostly low-boiling-point hydrocarbons, i.e. less than C₁₅, in the diesel and gasoline-range compounds.

Bhosle (2015) aimed to determine the potential effects of processing delay. Fifteen samples were analyzed within 1-3 days and the results show significant S1 and S2 values. The same samples were analyzed after four weeks and subsequently after three months. Results show declining trends in S1 and S2 values with time. The experimental results indicate that sample holding time also demonstrates considerable effects on the final results when the S1 and S2 values are high. Furthermore, results also reflected the feasibility of using the archived samples as proxies for fresh samples for determining the rock properties. The samples that were processed and analyzed within one to three days show significant S1 and S2 values. In contrast, the same samples analyzed after four weeks and subsequently after three months show declining trends.

Chapter 3

Research Methodology

3.1 Methodology

Core samples are selected from two vertical wells H and Q. The geographical distance between the two wells is approximately 150 km. Three feet of conventional core were used in this study. Two feet of core (Core 1 and Core 2) were from one well H, and the third foot (Core 3) is from well Q. The cores are sealed and preserved with three main layers, i.e., plastic wrap (three layers, 46 cm wide, approx. 1 meter per 1 foot of core), aluminum foil (two layers, 1 meter per sample), and then covered by CoreSeal® wax (1 kg per 1 ft.) (Figure 1) The preservation process performed in those three feet of the core material is considered a common practice for core preservation in the E & P industry.

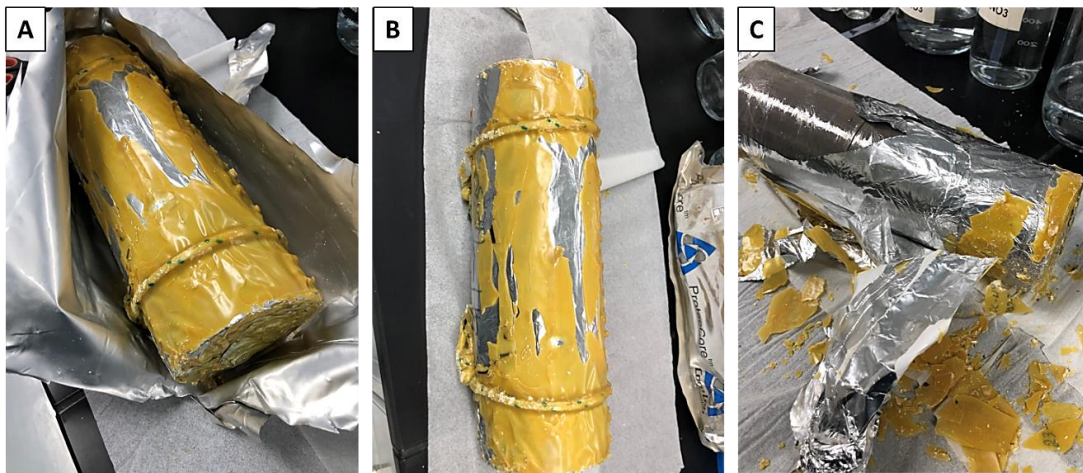


Figure 1: Example of 1 foot of conventional core used during this study. A & B: the core conditions when it was opened. Core was completely covered by wax layers. C: after removing the wax. The core is wrapped completely with aluminum foil that is followed by plastic wrap.

Wells H and Q were drilled in the same year (i.e. Jan 2020) (Table 1). They were pulled out from the subsurface, cut into 1-foot core samples, properly labeled, and immediately handled and preserved. The cores were completely enfolded, covered with plastic and aluminum then three times dipped into the melted wax. The cores were then placed in transport boxes and shipped to be stored at normal conditions in a shaded core store.

Table 1: Drilling and coring dates and storage duration.

Well ID	Core #	Drilling Date	Storage Duration after Drilling (Preserved)
Well H	1	Jan 2020	619 days
Well H	2	Jan 2020	634 days
Well Q	3	Jan 2020	661 days

During the selection process, pre-determined organic matter richness data and thermal maturity variations were considered. The core intervals from the same vertical well were selected to be in different organic richness levels based on the acquired wireline logs for the same depth interval. Gamma-ray and density with the help of sonic curves allowed the identification of organic-rich intervals (Well H, Core 1) and relatively leaner organic intervals (Well H, Core 2). Moreover, a slight difference between the two wells was encountered from a basin model exercise supported by ground truth subsurface samples from offset wells. Well H is slightly higher in thermal maturity (465-470 T_{MAX} -wet gas window) than well Q (455-460 T_{MAX} - volatile oil window). (Table 2)

Table 2: Organic richness and thermal maturity details of preserved cores. Thermal maturity and TOC ranges were obtained from previous pyrolysis measurements from un-preserved core samples.

Well ID	Core ID	Organic Richness (TOC %)	Thermal Maturity (T_{MAX})
Well H	1	4.0 - 10.0	465-470
Well H	2	2.0 - 4.0	465-470
Well Q	3	3.0 - 6.0	455-460

Consistent laboratory conditions, including sample selection and preparation, instrument selection and calibration were considered in reducing measurement uncertainty and for standardization purposes. Time is critical during this procedure to avoid overexposure and losing the light components. Therefore, the instrument was calibrated with the standard before each run, a clean area was set for sampling, a timer was set, tools were prepared, and the date and room temperature were reported.

239 samples were acquired from three different cores during this study. From each core, 75-85 samples were tested for pyrolysis, including the outer core surface samples. From each core, the samples were taken from locations identified prior test to ensure a consistent sampling protocol. Sample preparation included: manually drilling four samples using a metal file, labeling the sample, cleaning the tools after each run, storing the powdered sample in glass vials, and running samples into the RE7 instrument. The time at the beginning and completion of the sample was reported across all time-cycle runs during this study.

The core after samples were left opened, uncovered, and carried out to an indoor core store to avoid lab contamination. Other factors that could influence evaporation and losing light hydrocarbon are humidity, pressure, and temperature. Temperature is closely related to the energy content of fluid molecules, and increases in temperature

increase the ability for vaporization into the air. Warmer ambient air temperature has a greater capacity to hold vapor. Therefore, the lab and sample store temperatures forecast were also reported on a daily base and highlighted mainly for each run to support any further analysis or interpretation needs.

3.2 Lab Instrument

The pyrolysis technique is a commonly used industry practice to measure maturity. Pyrolysis instruments subject a crushed source rock sample to a programmed ramped temperature heating cycle that ramps progressively to measure the hydrocarbons and carbon dioxide released or generated by the sample during the run. Through the pyrolysis run, during the first isotherm phase (300°C), the resulting pyrograms show the free hydrocarbons (S1-peak; thermally vaporized or combusted) which are the hydrocarbons that have already been generated in situ, prior to pyrolysis, and are held within the source rock. The hydrocarbons associated with this phase are designated as S1 and are reported as milligrams of hydrocarbons per gram of rock (mgHC/g Rock). Theoretically, if a source rock sample is thermally immature, no thermally derived hydrocarbons will be measured during this step. This is because that source rock has not exceeded the energy threshold to initiate the maturation process of breaking hydrocarbon chains. The second temperature ramp phase is between 300 to 600°C. This is where the thermal cracking of kerogen and large molecular weight hydrocarbons within the source rock occurs. The rapid temperature increase induces the source rock to instantaneous thermally mature during the pyrolysis procedure. The measured hydrocarbons that are generated during this phase are called S2 and are also reported as

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mg HC/g Rock. Furthermore, T_{Max} is the term used for the temperature at which the maximum rate of hydrocarbon generation occurs in a kerogen sample during pyrolysis analysis (at the S2 peak). This T_{Max} is widely used as a thermal maturity parameter for source rock. Furthermore, during the thermal decomposition of the kerogen, the process of induced instantaneous thermal maturity generates CO_2 during the ramped phase. This CO_2 is held in a trap until the third phase which is the cooling phase, where it is once more released and measured. This is called S3 and is reported as mg CO_2 / g Rock (Peters et al., 2005a; Peters et al., 2005b). Finally, S4 represents the amount of residual carbon, measured through the yield of carbon dioxide and carbon monoxide that is produced by oxidation after the completion of pyrolysis. It is measured in mg CO_2 /g rock and mg CO/g rock.

There are several commercial brands and different pyrolysis instruments commercially available, including Rock Eval-II, Rock Eval-VI, Rock-Eval VII Source Rock Analyzer (SRA), and HAWK. Since the commercialization of rock eval apparatus in 1996, the Rock-Eval technology has become a standard reference to screen the petroleum potential in many research studies and daily operations for multiple advantages (Espitalié et al. 1977). A comparison has been done between TOC measured by the Rock-Eval instrument and by the Leco apparatus. The results display a good correlation when comparing elemental analyses and Rock-Eval for source rocks and kerogens. However, a comparison of Rock-Eval 6 with Leco data leads to larger deviations while correlation factors are still good. Several interlaboratory comparison studies (Dembicki, 1984; Magoon and Claypool, 1985; Rullkötter et al., 2001; Isaacs, 2001) have shown high variability in source rock geochemical results between different laboratories using

different instruments. Reported standard deviations in these studies have often been over 50%, even for basic source rock parameters like TOC, S1, and S2. In contrast, data from individual laboratories show relatively narrow ranges of standard error in source rock parameters (Birdwell, 2019).

A recent new technological invention has made it possible to characterize sulfur in tandem with hydrocarbons, CO₂, and CO. This is a new version of Rock-Eval (Rock-Eval 7S) that was developed to be run based on an open system to oxidize the rock after pyrolysis, unlike the earlier technological versions that were an open system with an online flame ionization detector. Rock-Eval 7 allows the characterization of total sulfur content in tandem with hydrocarbons, CO₂, and CO (Lamoureux-Var, 2019).

Rock-Eval 7S comprises two main furnaces, one for pyrolysis and the other for oxidation. During pyrolysis, part of the effluents passes through a combustion oven connected to the pyrolysis furnace, where the sulfur compounds are converted to SO₂. Through UV spectrometer, SO₂ can be detected, while the hydrocarbons and CO/CO₂ are detected respectively by the FID and IR spectrometer. After pyrolysis, the residue of pyrolysis is oxidized in the oxidation furnace. The released SO₂, CO, and CO₂ are detected respectively by the UV and IR spectrometers. The twin furnace design (pyrolysis and oxidation) is necessary to allow the formation of a permanent carbonaceous coating at the inner pyrolysis furnace surface. This coating, which is oxidized in single furnace machines, prevents further adsorption and subsequent loss of hydrocarbons interfering with hydrocarbon values (S1 and S2 peaks of the FID). This design also prevents unwanted oxidation of hydrocarbons condensed on the splitter outlet directed towards the CO/CO₂ line. The comparison of carbon and sulfur contents

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measured by Rock-Eval 7S and by elemental analysis showed an excellent correlation. In addition, the calibration of the device, separately in pyrolysis and oxidation, makes it possible to quantify the sulfur content released during pyrolysis (the ‘pyrolysis sulfur content’) and the residual sulfur content. The ‘pyrolysis sulfur’ in rocks, bitumen and sulfur-rich oils is interesting information as it is likely the source of organo-sulfur compounds and H_2S that are yielded upon geological or anthropic thermal processes. It is also possible to quantify the organic sulfur associated with the S1 and S2 peaks of the FID. The data processing software makes it possible to simulate, in addition to the cracking kinetics of the organic matter, the cracking kinetics of its organo-sulfur functions. This can help decipher the thermal cracking of sulfur-rich kerogens and source rocks. The superposition of the SO_2 and hydrocarbon signals helps discriminate the organic sulfur, which is associated with the S1 and S2 peaks of the FID, and the pyritic sulfur. However, the presence of clays and/or carbonates in rocks induces chemical reactions with sulfur compounds during the analysis, which can be detrimental to the interpretation of the signals. In this case, an estimation of pyritic sulfur and organic sulfur contents can be obtained via a mathematical model based on parameters derived from the Rock-Eval 7S analysis (Aboussou, 2018).

3.3 Experimental Design

Cores were preserved, sealed, covered and stored at room temperature before transferring to the core laboratory. A time schedule is set for each core to meet the planned time cycles, and to ensure instrument availability in a reasonable timeline and suitable time frame for the technician. Each core was run individually. During the

experiment, the core was unwrapped quickly and carefully to avoid any contamination during sample preparation. After removing the wax layers, both the aluminum and plastic covers were taken out quickly and carefully to avoid any contamination during sample preparation (Figure 1). Sandpaper was used to clean the surface of the sample to remove remnants of drilling mud. The powder that is obtained from the sandpaper treatment was collected in a glass-sealed vial and immediately ran in the Rock-Eval 7S Equipment for pyrolysis. The remaining sample is kept in the same glass vial for further analysis. After that, the one-foot core is labeled in four locations to ensure consistent sampling locations (10 cm apart from each sample). 40-50 grams were drilled and powdered from each sample location by a metal file (2 cm deep into the core). The metal file was used slowly to avoid any heat generation and cleaned with chemo papers after each sampling procedure to avoid contamination and mixing between samples. Samples were collected as a powder in sealed glass vials and immediately run by Rock-Eval for pyrolysis. Those samples are reported as fresh samples with 0 hour of residence time prior to analysis (Table 3).

Table 3: Time cycles for Core 1. Those time cycles include fresh samples; samples after 1 hour, 2 hours, 3 hours, 24 hours, 48 hours, 72 hours, 1 week, 2 weeks. Similar time-line was applied for Core 2 and Core 3.

Year	Day	Date	Core ID	Run ID	Sample Preparation Time	Sample Running Time
2022	Sunday	11-Sep	C1	Core Open	11:00:00 AM	
	Sunday	11-Sep	C1	Surface	11:00:00 AM	11:03:00 AM
	Sunday	11-Sep	C1	0h	11:05:00 AM	11:15:00 AM
	Sunday	11-Sep	C1	1h	12:15:00 PM	12:18:00 PM
	Sunday	11-Sep	C1	2h	1:18:00 PM	1:22:00 PM
	Sunday	11-Sep	C1	3h	2:22:00 PM	2:27:00 PM
	Monday	12-Sep	C1	24h	11:15:00 AM	11:24:00 AM
	Tuesday	13-Sep	C1	48h	11:24:00 AM	11:30:00 AM
	Wednesday	14-Sep	C1	72h	11:30:00 AM	11:35:00 AM
	Sunday	18-Sep	C1	1W	11:35:00 AM	11:38:00 AM
	Sunday	25-Sep	C1	2W	11:38:00 AM	11:45:00 AM

The remaining powdered samples are kept as backup samples and stored in the same labeled glass vials for any future investigations. The times when the measurement started and when the sample was inserted into the instrument were reported for each run. After that, the core was stored again unsealed at room temperature. After passing one hour, four more samples were collected from the same sampling locations and immediately run for pyrolysis. The same procedure is repeated after two hours and three hours for the same core. By finishing the three hours runs, the sample was completely uncovered and stored in the core store at room temperature pending for the next day for the 24-hour run. The protocols were repeated for the planned time cycles and for the other stored cores.

Those time cycles include fresh samples (0h); samples after 1 hour (1h), 2 hours (2h), 3 hours (3h), 24 hours (24h), 48 hours (48h), 72 hours (72h), 1 week (1W), 2 weeks (2W), 3 weeks (3W), 1 month (1MN), 2 months (2MN), 3 months (3MN), 4 months (4MN) and 5 months (5MN) (Table 3). Results from each run were plotted to determine the effects of sample storage time and analytical delays after sample extraction from the well. Furthermore, existing pyrolysis measurements from unpreserved core samples from the same cored wells were compared with those obtained from the preserved cores. (Figure 2)

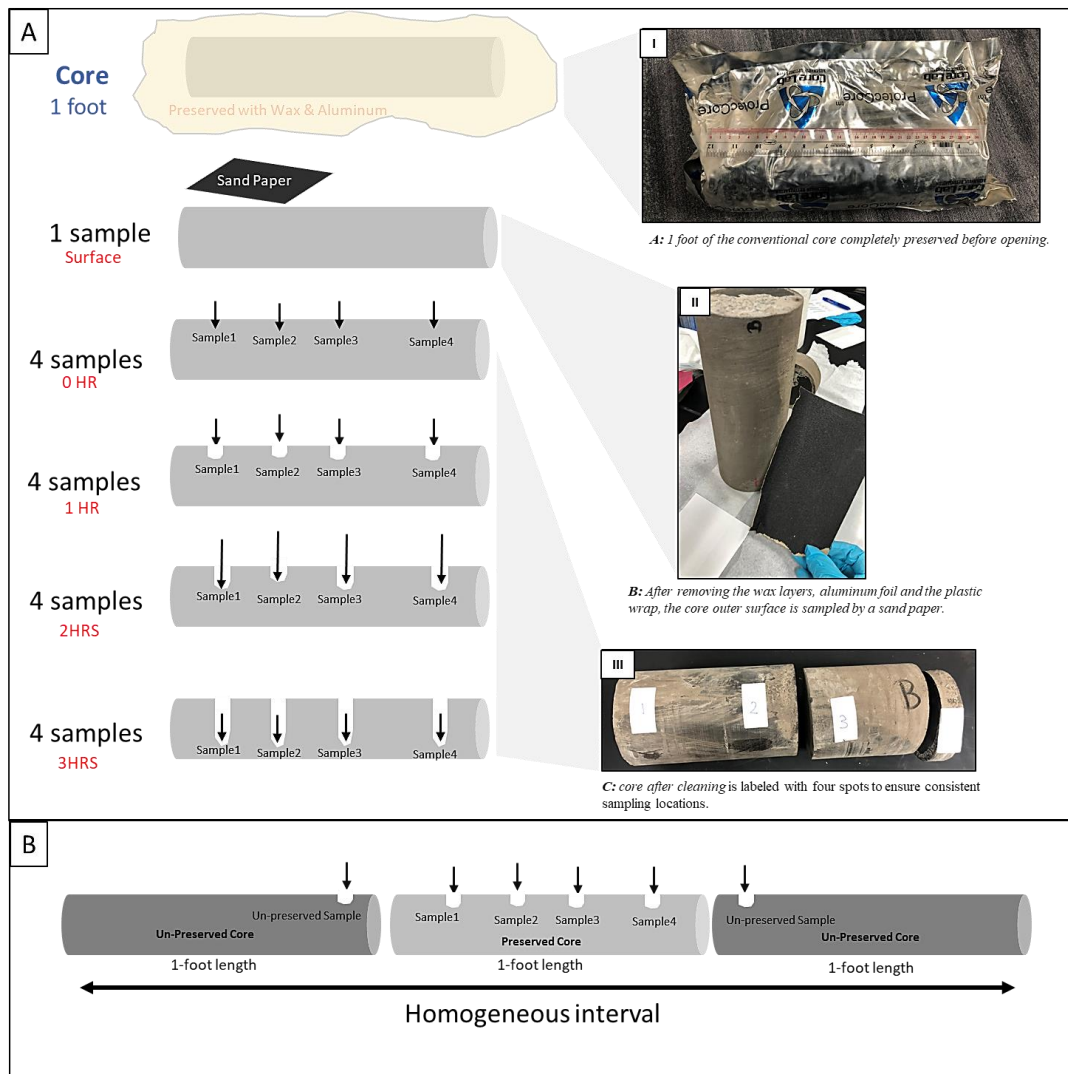


Figure 2 A: Sketch showing the conditions of the preserved cores and the location of the four samples collected. I: Cores are completely preserved. During the experiment, the core was unwrapped quickly, and II: sandpaper is used to manually remove the surface's outer layers. III: after that, the one-foot core is labeled with four spots (10 cm apart from each sample). The time cycles include fresh samples; samples after 1 hour, 2 hours, 3 hours, 24 hours, 48 hours, 72 hours, 1 week, 2 weeks, 3 weeks, 1 month, 2 months, 3 months, 4 months, and 5 months. B: Sketch shows the location of the samples measured from the un-preserved core intervals. Those sample measurements were obtained as the data set from the un-preserved core intervals.

3.4 Standards and Instrument Calibration

Instrument calibration is an essential stage in measurement procedures to ensure data reliability and repeatability. It is comprised of a set of operations that establish the relationship between the output of the measurement system and the accepted values of the calibration standards. This typically involves the preparation of a set of standards containing a known amount of the analyte of interest, measuring the instrument response for each standard and establishing the relationship between the instrument response and analyte concentration.

In order to improve the reliability and accuracy of the analysis equipment, a reference sample has been used at regular intervals. The standard samples used in this study were sourced from Vinci Technologies (IFP 160000 Standard), covering broad ranges of sulfur and carbon contents. The reference samples are certified by IFPEN (Institute Francais du Petrole Energies Nouvelles).

The IFP 160000 sample is taken from a homogeneous immature rock (Albian/Aptian marl), 180-120 μm . The S1 and S2 peaks are recorded at a standardized value of 0.14 mgHC/g TOC with 0.07 uncertainty and 12.43 mgHC/g TOC with 0.50 uncertainty. T_{MAX} is 416°C with $\pm 2^\circ\text{C}$ uncertainty, and TOC is 3.28% with a 0.14% uncertainty. The uncertainty is taken at the 99.7% confidence interval of the mean in the certified value. In order to ensure consistency in measuring results, the IFP 160000 standard samples have been analyzed during this study before each run (average 5 samples per run).

Measurement devices typically have specifications for their measurement ranges, accuracies and uncertainties. Overall, RockEval pyrolysis results (S1, S2, T_{MAX}, TOC) show very consistent results when comparing results from the same rock and the same instrument. Standard results from this study showed negligible differences across the pyrolysis parameters. S1 values from the standard are very similar with ± 0.07 mgHC/g. Also, S2 from the same IFP 160000 standard shows ± 0.01 mgHC/g difference, which is in the range of the accepted variance. Furthermore, T_{MAX} was 416°C across the different standard runs as expected. Additionally, TOC measurements are also comparable with a low variance of $\pm 0.32\%$ (Table 4).

As part of the best practices, testing the instrument (Rock-Eval) for consistency was accomplished by running duplicate samples randomly during the runs. Blind duplicate samples were run to evaluate sampling procedures and analytical equipment precision and accuracy. Core 1 results from samples No. 2 and No. 5 (Sample 2 and Sample 5) are identical with very consistent results. S1 and S2 values show deviations of ± 0.30 mgHC/g and ± 1.10 mgHC/g, respectively during this study. Measured TOC results look similar, with a variance of $\pm 0.3\%$. T_{MAX} values of both samples vary by $\pm 1.0^\circ\text{C}$. Similarly, Core 2 results show ± 0.18 mgHC/g for the S1 peak and ± 0.60 mgHC/g for the S2 peak. TOC measurements are $\pm 0.13\%$, while T_{MAX} is around $\pm 3.0^\circ\text{C}$. Also, Core 3 results show close values for S1 and S2 peaks with ± 0.28 mgHC/g and ± 0.72 mgHC/g respectively. TOC measurements are $\pm 1.0\%$ and T_{MAX} shows a very minor difference $< 5^\circ\text{C}$ (Table 5).

Table 4: IFP 160000 standard results. The standard materials used in this study were sourced from Vinci Technologies.

Analysis	Method	Cycle	Quantity (mg)	KfId	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	S4CO2 (mg/g)	S5 (mg/g)	Tmax (°C)	TpkS2 (°C)	PC (%)	RC (%)	TOC (%)	Total S (%)
STD	BULK ROCK	BASIC	53.70	2658.00	0.07	12.43	0.66	58.42	102.02	416.00	455.00	1.08	2.03	3.11	0.34
STD	BULK ROCK	BASIC	55.00	2617.00	0.07	12.43	0.67	58.10	101.56	416.00	456.00	1.08	2.02	3.10	0.34
STD	BULK ROCK	BASIC	52.90	2615.00	0.06	12.43	0.67	57.10	101.16	416.00	456.00	1.08	1.98	3.06	0.34
STD	BULK ROCK	BASIC	51.30	2530.00	0.06	12.43	0.64	58.25	102.88	416.00	455.00	1.08	2.02	3.10	0.34
STD	BULK ROCK	BASIC	51.20	2593.00	0.06	12.43	0.84	57.49	102.40	416.00	454.00	1.08	1.99	3.07	0.35
STD	BULK ROCK	BASIC	55.70	2578.00	0.07	12.43	0.73	58.13	101.08	416.00	455.00	1.08	2.02	3.09	0.33
STD	BULK ROCK	BASIC	52.50	2611.00	0.06	12.43	0.72	57.90	102.13	416.00	456.00	1.08	2.01	3.09	0.34
STD	BULK ROCK	BASIC	56.00	2495.00	0.46	12.43	0.85	56.35	100.76	416.00	450.00	1.12	1.96	3.08	0.35
STD	BULK ROCK	BASIC	54.60	2575.00	0.06	12.43	0.64	56.80	100.87	416.00	454.00	1.08	1.97	3.04	0.33
STD	BULK ROCK	BASIC	53.40	2622.00	0.06	12.43	0.71	57.16	100.88	416.00	455.00	1.08	1.98	3.06	0.35
STD	BULK ROCK	BASIC	56.70	2688.00	0.06	12.43	0.71	57.50	101.78	416.00	455.00	1.08	1.99	3.07	0.34
STD	BULK ROCK	BASIC	54.40	2670.00	0.06	12.43	0.71	56.39	99.86	416.00	453.00	1.08	1.96	3.04	0.33
STD	BULK ROCK	BASIC	54.60	2596.00	0.06	12.43	0.71	57.16	100.50	416.00	456.00	1.08	1.98	3.06	0.32
STD	BULK ROCK	BASIC	53.50	2609.00	0.07	12.43	0.67	56.71	100.77	416.00	454.00	1.08	1.97	3.05	0.33
STD	BULK ROCK	BASIC	50.70	2624.00	0.06	12.43				416.00	455.00	1.08	2.58	3.65	0.42
STD	BULK ROCK	BASIC	54.90	2565.00	0.07	12.43				416.00	455.00	1.08	2.46	3.54	0.39
STD	BULK ROCK	BASIC	55.00	2569.00	0.08	12.43				416.00	458.00	1.08	2.29	3.37	0.35
STD	BULK ROCK	BASIC	51.00	2634.00	0.08	12.43				416.00	455.00	1.08	2.51	3.60	0.38
STD	BULK ROCK	BASIC	52.20	4737.00	0.10	12.43				416.00	451.00	1.21	2.50	3.70	0.28
STD	BULK ROCK	BASIC	53.10	2584.00	0.09	12.43				416.00	456.00	1.08	2.57	3.66	0.31
STD	BULK ROCK	BASIC	51.60	2603.00	0.06	12.43	0.78	57.53	100.99	416.00	454.00	1.08	2.01	3.09	0.35
STD	BULK ROCK	BASIC	56.1	2569	0.07	12.43	0.83	59.99	101.94	416	454	1.08	2.09	3.18	0.35
STD	BULK ROCK	BASIC	52.3	2610	0.07	12.43	0.73	59.49	101.95	416	453	1.08	2.08	3.16	0.36
STD	BULK ROCK	BASIC	52.4	2580	0.06	12.43	0.71	58.61	101.06	416	453	1.08	2.05	3.13	0.35
STD	BULK ROCK	BASIC	52.3	2610	0.07	12.43	0.73	59.49	101.95	416	453	1.08	2.08	3.16	0.36

Table 5: Quality check tests - Sample 2 and Sample 5 results from the three cores.

Analysis	Sample	Quantity (mg)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	S4CO2 (mg/g)	S5 (mg/g)	Tmax (°C)	PI	HI	OH	Estimated Re	TOC (%)	Residual S (%)	Retained S (%)	Total S (%)
C1-3W-02	SAMPLE 2	55.20	3.91	7.86	0.34	213.46	270.87	467.00	0.33	85.00	4.00	1.17	9.19	0.86	0.21	1.37
C1-3M-02	SAMPLE 2	52.40	3.79	7.34	0.36	216.64	261.85	468.00	0.34	80.00	4.00	1.19	9.21	1.00	0.17	1.46
C1-3M-02	SAMPLE 2	52.10	3.57	7.54	0.43	284.63	353.87	470.00	0.32	65.00	4.00	1.22	11.65	1.01	0.21	1.47
C1-0M-02	SAMPLE 2	50.50	3.72	8.89	1.13	218.83	264.45	462.00	0.30	91.00	12.00	1.10	9.76	0.51	0.08	0.70
C1-5M-02	SAMPLE 2	50.4	3.48	7.45	0.41	217.00	263.55	471.00	0.32	81.00	4.00	1.24	9.22	0.90	0.18	1.52
C1-3W-05	SAMPLE 5	54.20	3.91	8.01	0.34	215.45	275.10	468.00	0.33	86.00	4.00	1.19	9.31	0.89	0.24	1.40
C1-3M-05	SAMPLE 5	52.00	4.01	8.14	0.47	221.97	269.20	467.00	0.33	86.00	5.00	1.18	9.45	0.95	0.18	1.44
C1-3M-05	SAMPLE 5	53.40	3.81	7.77	0.50	291.38	382.49	469.00	0.33	65.00	4.00	1.21	11.87	0.93	0.23	1.38
C1-0M-05	SAMPLE 5	56.40	3.23	7.49	0.31	227.58	261.89	471.00	0.30	79.00	3.00	1.24	9.53	1.11	0.19	1.76
C1-5M-05	SAMPLE 5	52.5	3.34	6.65	0.32	212.62	258.35	470.00	0.33	75.00	4.00	1.22	8.92	1.18	0.16	1.86
C2-0H-02	SAMPLE 2	52.5	2.19	5.09	0.94	68.68	321.35	388	0.3	166	39		3.07	0.04	0.23	0.31
C2-0H-02	SAMPLE 2	54.3	2.31	3.03	0.42	70.83	347.54	466	0.43	100	14	1.17	3.03	0.07	0.21	0.31
C2-3W-02	SAMPLE 2	52.7	1.96	2.85	0.41	71.05	344.9	469	0.41	96	14	1.22	2.96	0.03	0.21	0.26
C2-0M-02	SAMPLE 2	53.7	1.73	2.72	0.46	73.02	352.10	468.00	0.39	91.00	15.00	1.20	3.00	0.03	0.20	0.29
C2-0H-05	SAMPLE 5	52.6	2.34	2.93	0.44	68.42	351.19	466	0.44	99	15	1.17	2.94	0.06	0.14	0.38
C2-0H-05	SAMPLE 5	50.6	2.13	2.92	0.39	70.91	350.98	467	0.42	97	13	1.18	3	0.05	0.2	0.29
C2-3W-05	SAMPLE 5	53.3	1.9	2.72	0.33	70.62	349.96	472	0.41	92	11	1.25	2.96	0.04	0.17	0.33
C2-0M-05	SAMPLE 5	55.7	1.71	2.67	0.42	74.48	354.24	467.00	0.39	87.00	14.00	1.17	3.06	0.03	0.18	0.28
C3-24H-02	SAMPLE 2	51.3	3.36	6	0.74	109.86	343.3	480	0.36	132	16	1.06	4.55	0.01	0.2	0.31
C3-1W-02	SAMPLE 2	51.8	3.25	6.18	0.77	156.45	482.6	455	0.34	99	12	0.99	6.25	0	0.22	0.3
C3-2W-02	SAMPLE 2	41.3	3.23	5.61	0.55	114.80	403.34	458	0.37	116	11	1.03	4.85	0	0	0.05
C3-2M-02	SAMPLE 2	51.6	5.51	10.56	0.46	118.39	423.05	465	0.34	187	8	1.15	5.63	0.01	0.2	0.35
C3-0M-02	SAMPLE 2	53.7	1.73	2.72	0.46	73.02	352.10	468.00	0.39	91.00	15.00	1.20	3.00	0.03	0.20	0.29
C3-24H-05	SAMPLE 5	53.1	3.36	6	0.49	102.98	354.27	464	0.36	134	11	1.12	4.49	0.01	0.26	0.36
C3-1W-05	SAMPLE 5	48	3.18	5.66	0.6	128.03	456.77	457	0.36	107	11	1.01	5.27	0.01	0.22	0.29
C3-2W-05	SAMPLE 5	22.4	3.1	4.89	0.52	112.69	388.69	458	0.39	103	11	1.03	4.74	0	0.05	0.09
C3-2M-05	SAMPLE 5	51.8	5.23	10.52	0.38	114.95	426.48	468	0.33	188	7	1.19	5.58	0.02	0.26	0.37
C3-0M-05	SAMPLE 5	55.7	1.71	2.67	0.42	74.48	354.24	467.00	0.39	87.00	14.00	1.17	3.06	0.03	0.18	0.28

Chapter 4

Results

4.1 Sample Description and Mineralogy

Samples used in this study consist predominantly of marine carbonates and are primarily composed of laminated organic-rich mudstone. Samples are generally of calcareous nature with fine to medium grain size. They are rich in organic matter with observable bioturbation for the most part. Furthermore, sedimentary structures include gently undulating parallel lamination or sinuous lamination; cross lamination; ripple lamination, and micro-topographic infill lamination were observed in the study samples. Some samples were observed to have faintly-lamination, with minor anhydrite nodules and horizontal micro-burrows. The measured TOC shows an average of 5 wt% in the study samples. Additionally, some parts of the core's samples are light in color, have high illite concentration, highly cemented concretion with calcite, and show low organic contents (Figure 3).

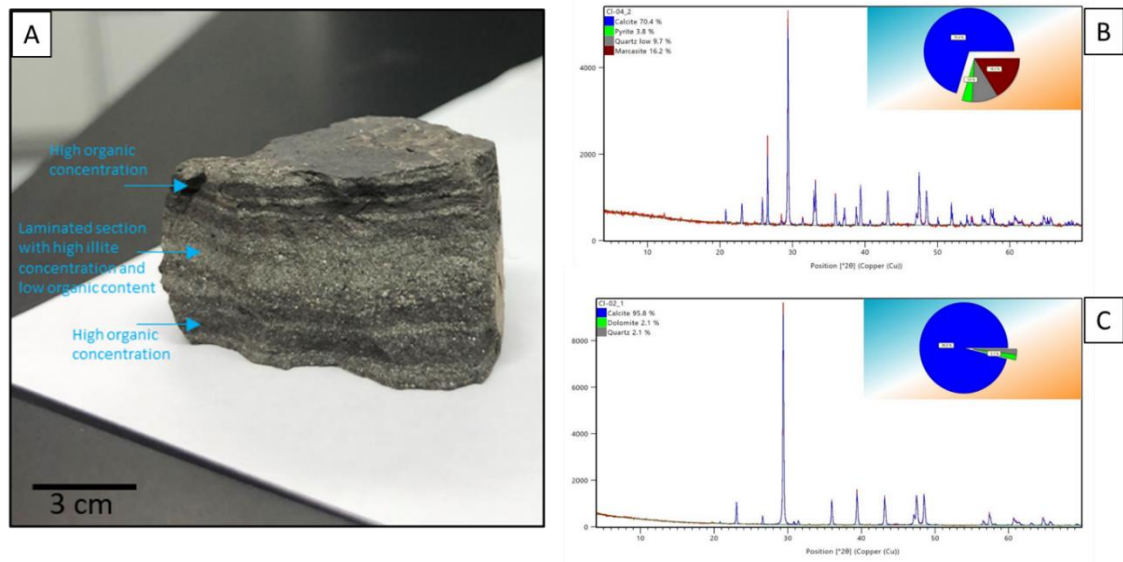


Figure 3: A: Rock sample from Core 1 composed of laminated organic-rich mudstone a laminated, light in color, high muscovite concentration, concretion, highly calcite cemented and low organic section. B: X-Ray Diffraction (XRD) results from Core 1 show that calcite forms the highest fraction (70%), indicating a relatively compositionally homogenous sample. C: X-Ray Diffraction (XRD) results from Core 2 show that Calcite forms 95 % in Core 1 in the samples, indicating a compositionally homogenous sample.

X-Ray Diffraction Analysis (XRD) and X-Ray Fluorescence (XRF) results from Core 1 and Core 2 show that calcite is the dominant component in the samples. The calcite distribution ranges from 70% to 96% by volume. The Pyrite distribution shows lower values with an average of 4%. Dolomite occurs in low amounts and with 2%. The quartz content is relatively low, ranging from 2% to 10% (Figure 3). In addition, X-Ray Fluorescence results (XRF) show high concentration of Calcium (Ca) with an average of 51% in Core 1 and relatively higher in Core 2 with an average of 90% (Table 6).

Table 6: X-Ray Fluorescence (XRF) from both Core 1 and Core 2.

	Al	Si	S	K	Ca	Ti	Fe	Ni	Zn	Sr
C1- Sample	1.70	6.45	23.01	0.14	43.59	0.23	24.60	0.01	0.19	0.09
C1- Sample	2.67	5.61	11.47	0.24	58.31	2.12	18.54	0.02	0.96	0.04
C1- Sample	1.45	3.15	20.12	0.04	52.15	0.53	21.56	0.01	0.87	0.12
C2- Sample	2.82	4.79	1.61	0.59	88.48	0.35	1.26	0.01	0.03	0.05
C2- Sample	2.79	4.75	1.55	0.60	88.45	0.29	1.43	0.01	0.01	0.11
C2- Sample	2.21	3.75	1.32	0.47	91.11	0.20	0.75	0.01	0.01	0.16

4.2 Pyrolysis Results from Preserved Cores

4.2.1 Pyrolysis Results from Core 1

Each preserved core is run individually for pyrolysis through consistent time cycles (Table 3). Results from each run is shown and plotted in this chapter to determine the effects of sample storage time and analytical delays after sample extraction from the well. The first core section from well 1 was opened on September, 11th, 2022 for the first lab run. 17 samples in total were taken from this core on the first day for the assigned lab runs (Figure 2). Those samples include the sample taken from the outer surface sample and the following time-cycles runs: 0h, 1h, 2h, and 3h (Table 3). Those runs are followed by the next tests in the following days as planned. In total, 64 samples are acquired from Core1 (1-foot length) (Table 7). Core 1 was tested for up to 5 months-time cycles following the planned time-cycles runs and is exposed (unpreserved) for 155 days since it was opened. The core is stored in a period with gradually decreasing weather temperature that is ranged from 45°C to 14°C (outside weather temperature) with an average of 30°C (Figure 4).

Figure 4: Core 1 storing temperature forecast. Average outside temperature is 30°C.

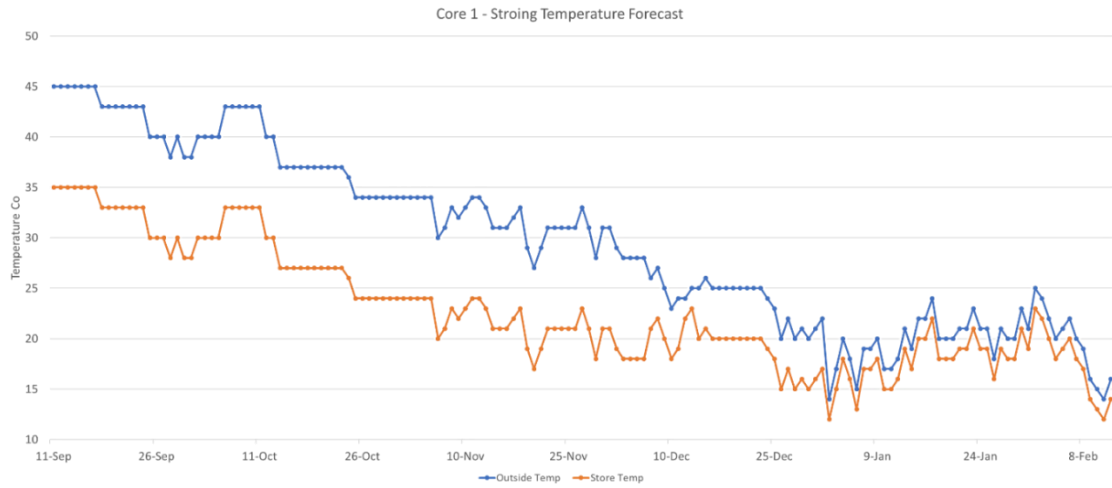


Table 7: Core 1 pyrolysis results.

Analysis	Sample	Method	Quantity (mg)	KfId	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	S4*CO (mg/g)	S5 (mg/g)	Tmax (°C)	PI	HI	OI	Estimated Ro	PC (%)	RC (%)	TOC (%)	Residual S (%)	Retained S (%)	Sulfate S (%)	Total S (%)
C1-0H-SURF	C1-0H-SURF	BULK ROCK	55.0	2609.0	4.21	11.44	2.38	0.06	139.82	389.00	0.77	182.00	39.00		1.41	4.70	6.11	0.32	0.00	0.00	0.42
C1-0H-01	SAMPLE 1	BULK ROCK	51.1	2609.0	4.20	7.84	0.54	1.02	295.95	470.00	0.37	104.00	7.00	1.73	1.07	6.47	7.54	0.64	0.37	0.01	1.10
C1-1H-01	SAMPLE 1	BULK ROCK	53.2	2609.0	4.32	7.39	0.40	0.96	292.31	469.00	0.37	99.00	5.00	1.71	1.00	6.45	7.45	0.59	0.28	0.08	1.01
C1-2H-01	SAMPLE 1	BULK ROCK	50.8	2596.0	4.12	7.36	0.40	0.86	284.44	466.00	0.36	94.00	5.00	1.16	0.98	6.86	7.83	0.58	0.30	0.00	0.95
C1-3H-01	SAMPLE 1	BULK ROCK	54.2	2596.0	3.12	5.37	0.77	0.84	276.50	469.00	0.37	95.00	5.00	1.71	0.77	4.96	5.68	0.47	0.31	0.00	0.85
C1-24H-01	SAMPLE 1	BULK ROCK	53.6	2670.0	4.87	7.27	0.36	1.00	295.21	470.00	0.39	94.00	5.00	1.72	1.00	6.05	7.85	0.59	0.73	0.08	0.96
C1-48H-01	SAMPLE 1	BULK ROCK	51.2	2670.0	4.89	7.08	0.47	0.91	289.05	468.00	0.39	95.00	6.00	1.19	0.98	6.49	7.47	0.54	0.27	0.00	0.89
C1-72H-01	SAMPLE 1	BULK ROCK	51.2	2688.0	4.80	7.54	0.57	0.88	296.74	470.00	0.39	99.00	7.00	1.72	1.05	6.55	7.60	0.57	0.73	0.07	0.94
C1-12W-01	SAMPLE 1	BULK ROCK	52.0	2575.0	4.62	7.27	0.58	0.94	295.40	466.00	0.39	96.00	8.00	1.16	1.01	6.56	7.57	0.58	0.25	0.03	1.03
C1-24W-01	SAMPLE 1	BULK ROCK	52.0	2575.0	4.62	7.27	0.58	0.94	295.40	466.00	0.39	96.00	8.00	1.16	1.01	6.56	7.57	0.58	0.25	0.03	1.03
C1-72W-01	SAMPLE 1	BULK ROCK	51.8	2495.0	4.31	7.01	0.53	0.88	293.37	471.00	0.38	97.00	7.00	1.74	0.97	6.62	7.59	0.55	0.74	0.07	0.91
C1-3W-01	SAMPLE 1	BULK ROCK	53.7	2530.0	4.32	7.35	0.48	1.08	293.52	465.00	0.37	97.00	6.00	1.15	0.99	6.57	7.55	0.62	0.31	0.03	1.10
C1-1MN-01	SAMPLE 1	BULK ROCK	53.3	2617.0	5.15	8.63	0.77	1.02	322.35	462.00	0.37	101.00	9.00	1.10	1.18	7.39	8.56	0.62	0.26	0.06	1.04
C1-2MN-01	SAMPLE 1	BULK ROCK	53.2	2569.0	4.37	7.17	0.52	1.18	383.51	470.00	0.38	77.00	6.00	1.72	0.98	8.29	9.27	0.66	0.35	0.01	1.15
C1-3MN-01	SAMPLE 1	BULK ROCK	52.8	2584.0	4.05	7.03	0.46	1.29	391.63	471.00	0.37	76.00	5.00	1.24	0.94	8.29	9.24	0.70	0.44	0.02	1.24
C1-4MN-01	SAMPLE 1	BULK ROCK	51.0	2604.0	3.68	6.97	0.40	0.93	288.59	469.00	0.35	93.00	5.00	1.21	0.90	6.62	7.53	0.62	0.31	0.01	1.13
C1-5MN-01	SAMPLE 1	BULK ROCK	51.2	2569.0	3.80	7.13	0.36	1.07	298.78	473.00	0.35	93.00	5.00	1.77	0.94	6.78	7.69	0.64	0.30	0.04	1.11
C1-0H-02	SAMPLE 2	BULK ROCK	52.7	2609.0	4.65	8.99	0.53	0.68	272.30	472.00	0.34	98.00	6.00	1.26	1.16	8.01	9.17	0.96	0.21	0.00	1.46
C1-1H-02	SAMPLE 2	BULK ROCK	54.0	2609.0	4.02	8.30	0.38	0.73	282.50	472.00	0.33	90.00	4.00	1.75	1.05	8.18	9.27	0.85	0.28	0.01	1.77
C1-2H-02	SAMPLE 2	BULK ROCK	54.9	2596.0	3.71	8.04	0.33	0.71	264.97	467.00	0.32	88.00	4.00	1.18	1.00	8.19	9.19	0.78	0.22	0.01	1.18
C1-3H-02	SAMPLE 2	BULK ROCK	53.4	2596.0	3.90	7.93	0.36	0.73	272.11	468.00	0.33	87.00	4.00	1.19	1.01	8.06	9.07	0.86	0.22	0.01	1.27
C1-24H-02	SAMPLE 2	BULK ROCK	53.6	2670.0	4.69	12.21	0.86	0.52	234.55	460.00	0.38	138.00	10.00	1.07	1.45	7.42	8.86	0.72	0.19	0.01	1.09
C1-48H-02	SAMPLE 2	BULK ROCK	54.0	2670.0	4.36	8.47	0.41	0.68	262.27	472.00	0.34	92.00	4.00	1.26	1.09	8.12	9.21	0.84	0.21	0.02	1.25
C1-72H-02	SAMPLE 2	BULK ROCK	51.6	2688.0	4.46	8.28	0.37	0.65	269.24	469.00	0.35	89.00	4.00	1.21	1.08	8.19	9.27	0.82	0.19	0.00	1.19
C1-12W-02	SAMPLE 2	BULK ROCK	50.9	2575.0	4.97	9.08	0.49	0.75	294.28	466.00	0.35	92.00	5.00	1.17	1.19	8.68	9.88	0.80	0.21	0.00	1.77
C1-24W-02	SAMPLE 2	BULK ROCK	50.9	2575.0	4.97	9.08	0.49	0.75	294.28	466.00	0.35	92.00	5.00	1.17	1.19	8.68	9.88	0.80	0.21	0.00	1.77
C1-72W-02	SAMPLE 2	BULK ROCK	55.1	2495.0	4.17	8.27	0.38	0.75	277.35	472.00	0.34	89.00	4.00	1.25	1.06	8.23	9.29	0.72	0.22	0.00	1.13
C1-3W-02	SAMPLE 2	BULK ROCK	55.2	2530.0	3.91	7.86	0.34	0.69	270.87	467.00	0.33	85.00	4.00	1.17	1.00	8.20	9.19	0.86	0.21	0.00	1.37
C1-1MN-02	SAMPLE 2	BULK ROCK	52.4	2617.0	3.79	7.34	0.36	0.54	261.85	468.00	0.34	80.00	4.00	1.19	0.95	8.26	9.21	1.00	0.17	0.01	1.46
C1-2MN-02	SAMPLE 2	BULK ROCK	54.2	2569.0	3.76	7.55	0.44	0.75	363.11	469.00	0.33	62.00	4.00	1.20	0.96	11.18	12.15	1.15	0.22	0.03	1.73
C1-3MN-02	SAMPLE 2	BULK ROCK	52.1	2584.0	3.57	7.54	0.43	0.72	353.87	470.00	0.32	65.00	4.00	1.72	0.95	10.70	11.65	1.01	0.21	0.01	1.47
C1-4MN-02	SAMPLE 2	BULK ROCK	50.5	2604.0	3.72	8.89	0.33	0.29	264.45	462.00	0.30	91.00	12.00	1.10	1.10	8.66	9.76	0.51	0.08	0.01	0.70
C1-5MN-02	SAMPLE 2	BULK ROCK	50.4	2569.0	3.48	7.45	0.41	0.55	283.55	471.00	0.32	81.00	4.00	1.74	0.93	8.29	9.22	0.96	0.18	0.01	1.52
C1-0H-03	SAMPLE 3	BULK ROCK	51.9	2609.0	2.50	2.68	0.57	0.96	354.98	459.00	0.48	90.00	19.00	1.04	0.46	2.53	2.99	0.44	0.17	0.00	0.67
C1-1H-03	SAMPLE 3	BULK ROCK	50.1	2609.0	2.37	3.02	0.63	0.85	348.70	462.00	0.44	101.00	21.00	1.09	0.48	2.53	3.00	0.32	0.17	0.01	0.54
C1-2H-03	SAMPLE 3	BULK ROCK	52.0	2596.0	2.01	1.82	0.53	0.98	360.00	452.00	0.52	72.00	21.00	0.93	0.34	2.17	2.52	0.37	0.16	0.00	0.59
C1-3H-03	SAMPLE 3	BULK ROCK	52.3	2596.0	2.02	2.07	0.52	1.10	341.45	457.00	0.49	77.00	20.00	1.01	0.36	2.31	2.67	0.37	0.18	0.02	0.62
C1-24H-03	SAMPLE 3	BULK ROCK	50.8	2670.0	1.94	1.96	0.60	1.01	354.05	455.00	0.50	81.00	25.00	0.99	0.35	2.07	2.42	0.35	0.16	0.00	0.56
C1-48H-03	SAMPLE 3	BULK ROCK	52.7	2670.0	1.90	1.95	0.48	1.04	349.08	459.00	0.49	78.00	19.00	1.04	0.34	2.17	2.51	0.46	0.19	0.01	0.72
C1-72H-03	SAMPLE 3	BULK ROCK	51.5	2688.0	2.18	2.29	0.54	1.05	354.93	454.00	0.49	82.00	19.00	0.96	0.40	2.40	2.79	0.46	0.19	0.00	0.70
C1-12W-03	SAMPLE 3	BULK ROCK	55.5	2575.0	3.86	4.43	1.17	0.50	319.36	450.00	0.47	109.00	29.00	0.89	0.73	3.33	4.07	0.17	0.17	0.01	0.41
C1-24W-03	SAMPLE 3	BULK ROCK	55.5	2575.0	3.86	4.43	1.17	0.50	319.36	450.00	0.47	109.00	29.00	0.89	0.73	3.33	4.07	0.17	0.17	0.01	0.41
C1-72W-03	SAMPLE 3	BULK ROCK	52.4	2495.0	4.03	4.29	1.13	0.61	318.79	455.00	0.48	104.00	28.00	0.98	0.74	3.38	4.12	0.29	0.16	0.01	0.53
C1-3W-03	SAMPLE 3	BULK ROCK	52.2	2530.0	3.21	3.74	1.01	0.75	323.04	452.00	0.46	101.00	27.00	0.93	0.62	3.09	3.71	0.32	0.16	0.05	0.59
C1-1MN-03	SAMPLE 3	BULK ROCK	51.6	2617.0	3.36	4.40	0.89	1.02	353.44	461.00	0.43	97.00	20.00	1.08	0.68	3.86	4.54	0.59	0.28	0.00	0.96
C1-2MN-03	SAMPLE 3	BULK ROCK	52.9	2569.0	3.01	3.42	0.85	1.20	441.05	460.00	0.47	69.00	17.00	1.07	0.57	4.42	4.98	0.52	0.27	0.01	0.86
C1-3MN-03	SAMPLE 3	BULK ROCK	51.0	2584.0	2.89	3.36	0.87	0.96	430.55	460.00	0.46	71.00	18.00	1.06	0.56	4.17	4.73	0.50	0.22	0.01	0.78
C1-4MN-03	SAMPLE 3	BULK ROCK	43.5	2604.0	2.22	2.79	0.78	0.85	329.03	456.00	0.44	83.00	23.00	1.00	0.45	2.92	3.37	0.53	0.18	0.00	0.79
C1-5MN-03	SAMPLE 3	BULK ROCK	51.4	2569.0	2.75	3.41	0.86	0.86	321.77	460.00	0.45	86.00	22.00	1.07	0.55	3.44	3.99	0.42	0.23	0.01	0.72
C1-0H-04	SAMPLE 4	BULK ROCK	54.8	2609.0	1.69	1.13	1.42	0.11	264.87	162.00	0.60	60.00	76.00		0.29	1.58	1.88	2.01	0.09	0.00	2.31
C1-1H-04	SAMPLE 4	BULK ROCK	56.8	2609.0	1.30	0.55	2.08	0.01	177.29	297.00	0.70	31.00	118.00		0.23	1.53	1.76	3.46	0.03	0.02	4.02
C1-2H-04	SAMPLE 4	BULK ROCK	54.7	2596.0	0.65	0.25	1.01	0.11	230.66	152.00	0.72	22.00	89.00		0.12	1.02	1.14	3.43	0.20	0.01	4.80
C1-3H-04	SAMPLE 4	BULK ROCK	51.4	2596.0	1.45	0.85	1.24	0.16	280.85	158.00	0.63	54.00	79.00		0.24	1.31	1.57	2.19	0.10	0.00	2.53
C1-24H-04	SAMPLE 4	BULK ROCK	51.8	2670.0	1.50	1.05	1.76	0.04	198.75	374.00	0.59	64.00	107.00		0.28	1.36	1.64	3.39	0.04	0.04	4.07
C1-48H-04	SAMPLE 4	BULK ROCK	54.0	2670.0	1.18	0.69	1.51	0.04	207.94	160.00	0.63	42.00	93.00		0.21	1.42	1.63	3.24	0.05	0.03	4.16
C1-72H-04	SAMPLE 4	BULK ROCK	53.2	2688.0	1.94	1.98	1.83	0.04	210.02	376.00	0.49	86.00	79.00		0.40	1.90	2.30	2.05	0.03	0.01	2.37
C1-12W-04	SAMPLE 4	BULK ROCK	53.0	2575.0	1.13	0.56	1.11	0.12	249.68	432.00	0.67	37.00	74.00	0.57	0.18	1.32	1.51	2.91	0.07	0.03	3.64
C1-24W-04	SAMPLE 4	BULK ROCK	53.0	2575.0	1.13	0.56	1.11	0.12	249.68	432.00	0.67	37.00	74.00	0.57	0.18	1.32	1.51	2.91	0.07	0.	

Through the different time-cycle runs up to 5 months, Core 1 results show no significant change in S1 values over time. S1 from the outer core surface that is sampled immediately after unwrapping the core shows 4.21 mgHC/g. This value comes close enough to S1 values for both Sample 1 and Sample 2 after cleaning the core with 4.36 mgHC/g and 4.18 mgHC/g, respectively. Unlikely, Sample 3 and Sample 4 show relatively lower S1 values with 2.8 mgHC/g and 1.0 mgHC/g, respectively. (Table 8).

Table 8: S1 data (mgHC/g) comparison between the outer core surface and the four core samples at 0h (fresh samples) from Core 1.

TIME	Surface	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4
0h	4.21	4.36	4.18	2.76	0.98

Generally, a minor change in S1 values for the four samples was observed over time. The difference between the average S1 during the first three runs and the last two runs is 0.59 mgHC/g in Sample 1. While Sample 2 and Sample 4 exhibit a difference between the runs of 0.53 mgHC/g, and 0.44 mgHC/g receptively. On the other hand, Sample 3 shows the least difference between runs in S1 with 0.19 mgHC/g (Table 9 & Figure 5).

Table 9: S1 data (mgHC/g) difference in Core 1 between the first three runs: fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 4 months, and after 5 months (4MN and 5MN) for the four samples.

SAMPLE ID	Avg (0h,1h and 2H)	Avg (4MN and 5MN)	Δ S1 (mg/g)	Δ %
SAMPLE 1	4.38	3.79	0.59	13.5
SAMPLE 2	4.13	3.60	0.53	12.8
SAMPLE 3	2.29	2.49	-0.19	-8.4
SAMPLE 4	1.13	0.70	0.44	38.7

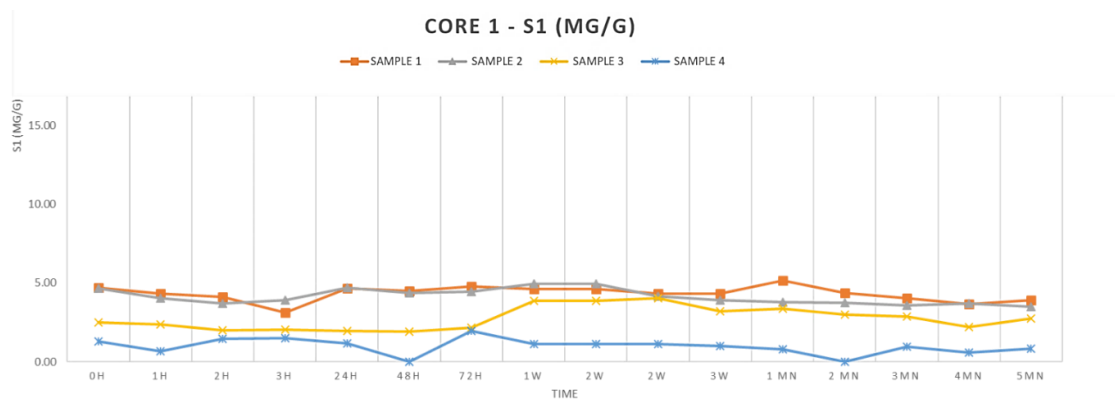


Figure 5: S1 (mgHC/g) change over time for the four samples from Core1. This core is tested for up to 5 months-time cycles.

In order to ensure data quality, duplicate samples were tested from Sample 2. Those samples are labeled as Sample 5 during three weeks run (3W), after the first month (1MN), after three months (3MN), after 4 months (4MN), and after 5 months run (5MN). Results show very minor differences in the S1 values for both samples (Sample 2 and Sample 5) (Table 10).

Table 10: S1 data (mgHC/g) quality check test (QC). Sample 2 and Sample 5 results from Core 1.

QC TEST	S1 (mg/g)				
SAMPLE ID	3W	1MN	3MN	4MN	5MN
SAMPLE 2	3.91	3.79	3.57	3.72	3.48
SAMPLE 5	3.91	4.01	3.81	3.23	3.34
Δ S1 (mg/g)	0.00	-0.22	-0.24	0.49	0.14
Δ %	100.0	105.8	106.7	86.8	96.0

For S2 values; Core 1 results show also no significant change within S2 values over the different time cycles. S2 from the outer core surface that is sampled immediately after unwrapping the core shows 11.44 mgHC/g. This value is incomparable with the other four samples. S2 values for both Sample 1 and Sample 2 after cleaning the core are 7.23 mgHC/g & 8.52 mgHC/g respectively. Unlikely, Sample 3 and Sample 4 show

relatively lower S2 values with 3.11 mgHC/g and 0.72 mgHC/g respectively (Table 11).

Table 11: S2 data (mgHC/g) comparison between the outer core surface and the four core samples at 0h (fresh samples) from Core 1.

TIME	Surface	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4
0h	11.44	7.23	8.52	3.11	0.72

Furthermore, a minor change in S2 values is observed over time. This S2 behavior is almost identical in the four samples from the same core. Average change in S2 values between the first three runs and the last two runs in the four samples show a minor decrease that is ranged from 0.21-0.48 mgHC/g except for Sample 3, which shows a slight increase with an average difference of 0.59 mgHC/g. Overall, S2 peaks exhibit no significant change over time in the four samples. (Table 12 and Figure 6).

Table 12: S2 data (mgHC/g) difference in Core 1 between the first three runs: fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 4 months, and after 5 months (4 MN and 5 MN) for the four samples.

SAMPLE ID	Avg (0h,1h and 2h)	Avg (4MN and 5MN)	Δ S2 (mg/g)	Δ %
SAMPLE 1	7.53	7.05	0.48	6.4
SAMPLE 2	8.44	8.17	0.27	3.2
SAMPLE 3	2.51	3.10	-0.59	-23.7
SAMPLE 4	0.64	0.43	0.21	33.2

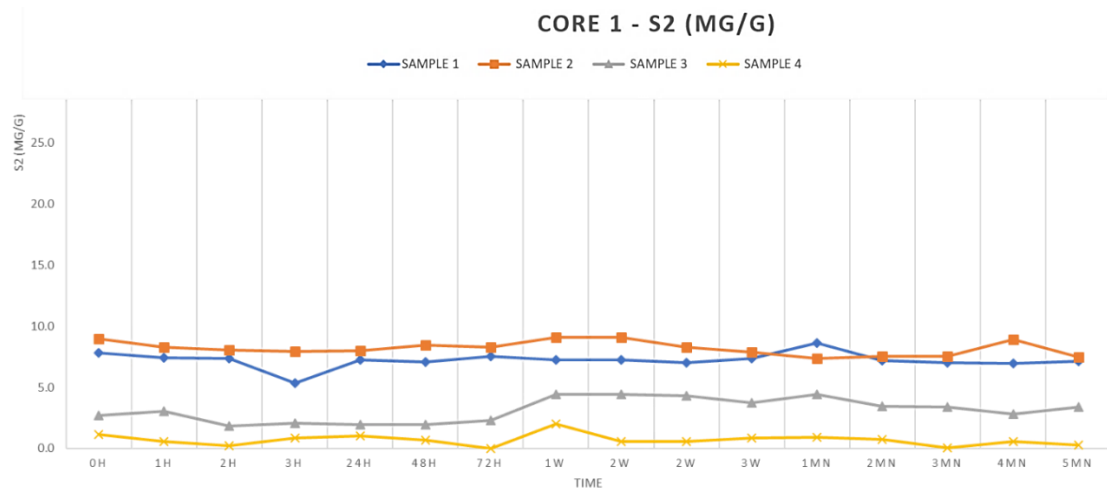


Figure 6: S2 (mgHC/g) changes over time for the four samples from Core 1. This core is tested up to 5 months-time cycles.

Similarly, duplicated samples were tested from Sample 2. The S2 values for both samples (Sample 2 and Sample 5) are within the accepted range (Table 13).

Table 13: S2 data (mgHC/g) quality check test (QC). Sample 2 and Sample 5 results from Core 1

QC TEST - S2 (mg/g)					
SAMPLE ID	3W	1MN	3MN	4MN	5MN
SAMPLE 2	7.86	7.34	7.54	8.89	7.45
SAMPLE 5	8.01	8.14	7.77	7.49	6.65
Δ S2 (mg/g)	-0.15	-0.80	-0.23	1.40	0.80
Δ %	101.9	110.9	103.1	84.3	89.3

Adding to this, T_{MAX} from Core 1 shows almost no changes over time. T_{MAX} from the outer core surface is 389°C. This value is not comparable with the other four samples. T_{MAX} values for Sample 1, Sample 2 and Sample 3 after cleaning the core are 468°C, 468°C, and 456°C, respectively. On the other hand, Sample 4 results show lower T_{MAX} values at 342°C, which is relatively close to the outer surface result (Table 14).

Table 14: T_{MAX} data (°C) comparison between outer core surface and the four core samples from Core 1 at 0h (fresh samples).

TIME	Surface	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4
0h	389	468	468	456	342

T_{MAX} behavior is almost identical for Samples 1, 2 and 3. Average T_{MAX} change for the first three runs and the last two runs is $\pm 4.0^{\circ}\text{C}$ for Sample 1, Sample 2, and Sample 3 respectively (Table 15). While Sample 4 exhibits outliers with T_{MAX} values over the different time runs. Average T_{MAX} value is 240°C for samples measured for up to 48 hours run, after that the values start to increase with an average of 430°C . The anomaly in T_{MAX} reading most likely is affected by the low TOC content in Sample 4. Sample 4 was taken from a laminated, light color, high illite concentration, highly cemented concretion with calcite and low organic section from Core 1. This sample shows lean to non-source rock facies that is fairly unrepresentative of Core 1 (Figure 7).

Table 15 T_{MAX} data ($^{\circ}\text{C}$) difference in Core 1 between the first three runs fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 4 months, and after 5 months (4MN and 5MN) for the four samples.

SAMPLE ID	Avg (0h,1h and 2h)	Avg (4MN and 5MN)	Δ Tmax ($^{\circ}\text{C}$)	Δ %
SAMPLE 1	468	471	-3	-1
SAMPLE 2	470	467	4	1
SAMPLE 3	458	458	0	0
SAMPLE 4	204	404	-200	-98

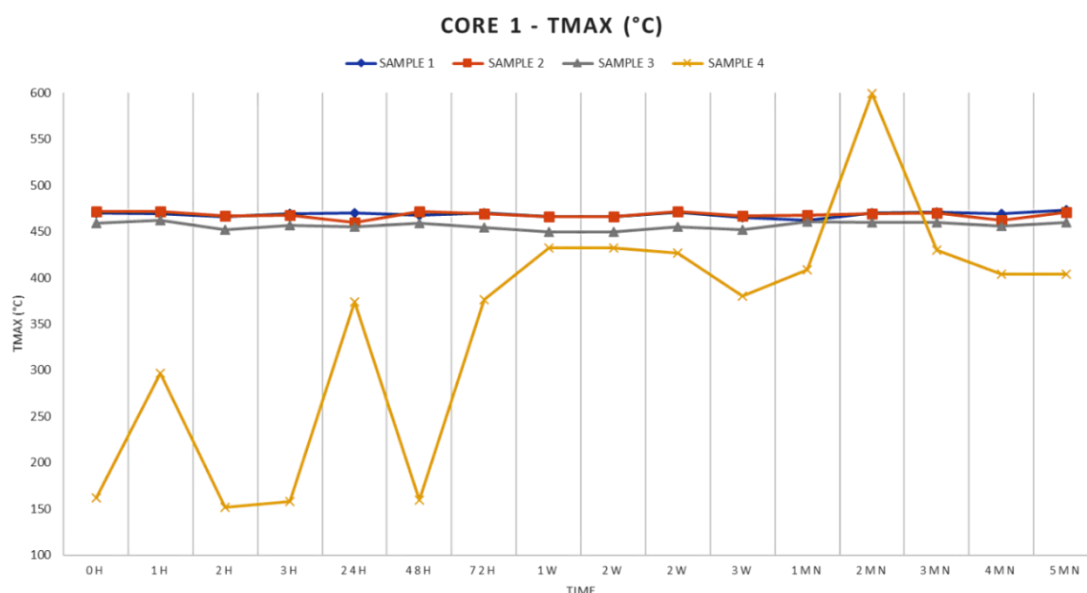


Figure 7: T_{MAX} (°C) change with time for the four samples from Core 1. This core is tested up to 5 months-time cycles. The anomaly in T_{MAX} reading most likely is affected by the low TOC content in Sample 4. Sample 4 was taken from a laminated, light in color, high illite concentration, highly cemented concretion with calcite and low organic section from Core 1. This sample shows lean to non-source rock facies that is fairly unrepresentative of Core 1.

The duplicated samples (Sample 2 and Sample 5) are within the accepted range of T_{MAX} change with $\Delta 1^\circ$ cover 4 tests except 4-month run that shows $\Delta 9^\circ\text{C}$ (Table 16).

Table 16: T_{MAX} data (°C) quality check test (QC). Sample 2 and Sample 5 results from Core 1.

SAMPLE ID	QC Test - Tmax (°C)				
	3W	1MN	3MN	4MN	5MN
SAMPLE 2	467	468	470	462	471
SAMPLE 5	468	467	469	471	470
Δ Tmax (°C)	-1	1	1	-9	1
Δ %	100	100	100	102	100

TOC measurements from the outer core surface show 6.11% TOC. This value is close to Sample 1 and Sample 2 which are 7.74% & 9.67% TOC, respectively. Sample 3 and

Sample 4 show relatively lower TOC values with 3.50% and 1.35% TOC respectively. (Table 17).

Table 17: TOC data (%) comparison between the outer core surface and the four core samples at 0h (fresh samples) from Core 1.

TIME	Surface	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4
0h	6.11	7.74	9.67	3.50	1.35

Overall, TOC measurements show minor changes. Average change for the four samples during the first three runs and the last two runs ranged from 0.1-0.84% TOC (Table 18), despite the TOC variation in the four samples. The TOC behavior through the different time cycles up to 5 months is almost identical in the four samples (Figure 8).

Table 18: TOC data (%) difference in Core 1 between the first three runs fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 4 months, and after 5 months (4MN and 5MN) for the four samples.

SAMPLE ID	Avg (0h,1h and 2h)	Avg (4MN and 5MN)	Δ TOC (%)	Δ %
SAMPLE 1	7.61	7.61	0.00	0.0
SAMPLE 2	9.19	9.49	-0.30	-3.2
SAMPLE 3	2.84	3.68	-0.84	-29.7
SAMPLE 4	1.59	1.48	0.11	7.1

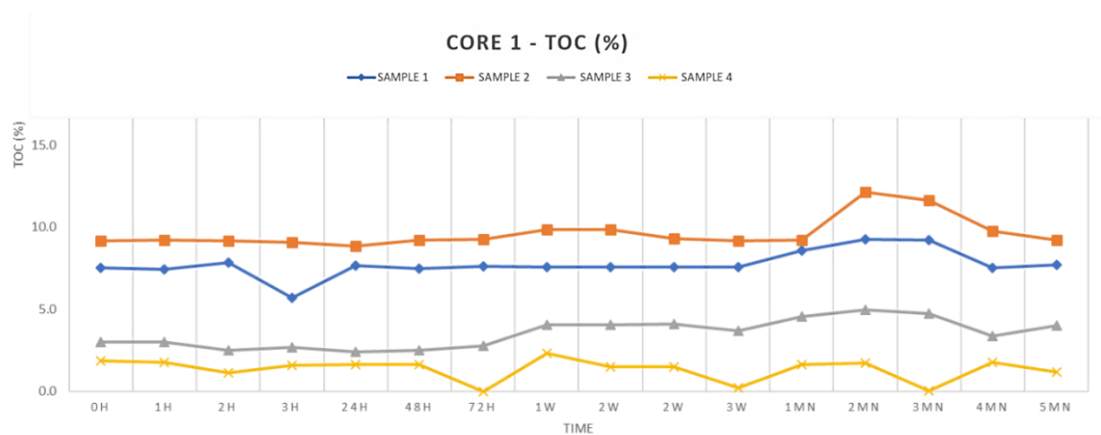


Figure 8: TOC (%) change with time for the four samples from Core 1. This core is tested for up to 5 months-time cycles.

And similarly, for the duplicated samples (Sample 2 and Sample 5). Results show minor differences with a maximum difference of $\Delta 0.3\%$ TOC during the five-time cycle tests (Table 19).

Table 19: TOC data (%) quality check test (QC). Sample 2 and Sample 5 results from Core 1

SAMPLE ID	QC Test - TOC (%)				
	3W	1MN	3MN	4MN	5MN
SAMPLE 2	9.19	9.21	11.65	9.76	9.22
SAMPLE 5	9.31	9.45	11.87	9.53	8.92
Δ TOC (%)	-0.12	-0.24	-0.22	0.23	0.30
Δ %	101.3	102.6	101.9	97.6	96.7

4.2.2 Pyrolysis Results from Core 2

Core 2 was opened on September, 26th (2022) for the first lab run. A total of 19 samples were acquired from this core on the first day for the assigned lab runs including the outer surface samples (Figure 2). Overall, 55 samples in total are collected from Core 2 (Table 20). Unlike Core 1, this core was tested over a 4 months-time timeframe and was exposed (unpreserved) for 121 days from opening. The core was stored in a gradually decreasing ambient temperature ranging from 43°C to 14°C (outside temperature) with an average of 29.5°C (Figure 9).

Figure9: Core 2 storing temperature. The average outside temperature is 29.5°C and the average store temperature is 22°C.

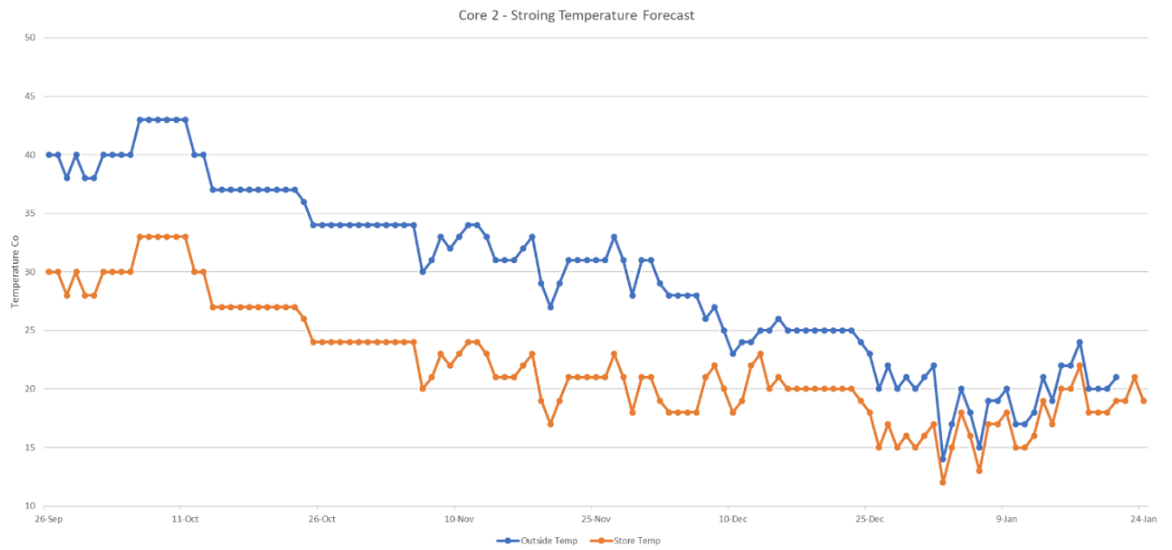


Table 19: Core 2 pyrolysis results.

Analysis	Sample	Method	Quantity (mg)	K2Ed	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	S4CO2 (mg/g)	S5 (mg/g)	Tmax (°C)	PI	HI	OI	Estimated Ro	PC (%)	RC (%)	TOC (%)	Residual S (%)	Retained S (%)	Sulfate S (%)	Total S (%)
C2-0H-SURF	C2-0H-SURF	BULK ROCK	55.6	2495.0	2.25	9.10	1.63	66.57	205.38	380.00	0.20	287.00	51.00		1.02	2.15	3.17	0.03	0.16	0.00	0.25
C2-0H-01	SAMPLE 1	BULK ROCK	55.4	2495.0	2.17	4.75	1.00	66.74	206.76	388.00	0.31	159.00	33.00		0.61	2.34	2.98	0.17	0.16	0.02	0.71
C2-1H-01	SAMPLE 1	BULK ROCK	52.7	2495.0	2.25	2.38	0.53	64.28	337.19	384.00	0.49	88.00	20.00		0.41	2.30	2.71	0.45	0.18	0.03	0.73
C2-2H-01	SAMPLE 1	BULK ROCK	51.2	2611.0	2.29	2.55	0.61	64.24	337.35	381.00	0.47	94.00	23.00		0.43	2.29	2.72	0.44	0.18	0.03	0.71
C2-3H-01	SAMPLE 1	BULK ROCK	54.3	2611.0	2.23	2.09	0.54	65.49	338.00	383.00	0.52	77.00	20.00		0.38	2.53	2.71	0.42	0.15	0.01	0.65
C2-4H-01	SAMPLE 1	BULK ROCK	51.3	2611.0	2.42	2.97	0.75	66.51	324.79	385.00	0.45	105.00	26.00		0.48	2.34	2.82	0.39	0.16	0.01	0.63
C2-4H-01	SAMPLE 1	BULK ROCK	51.8	2578.0	2.12	2.17	0.60	62.57	335.60	388.00	0.49	83.00	23.00		0.38	2.22	2.60	0.38	0.16	0.03	0.63
C2-72H-01	SAMPLE 1	BULK ROCK	51.8	2578.0	2.06	1.99	0.59	60.95	348.05	392.00	0.51	79.00	23.00		0.36	2.17	2.53	0.34	0.19	0.01	0.61
C2-1W-01	SAMPLE 1	BULK ROCK	51.9	2530.0	1.73	1.73	0.44	56.83	347.77	453.00	0.50	74.00	19.00	0.94	0.31	2.02	2.32	0.29	0.16	0.03	0.55
C2-2W-01	SAMPLE 1	BULK ROCK	52.5	2615.0	2.04	1.88	0.51	62.70	342.36	381.00	0.52	73.00	21.00		0.35	2.25	2.58	0.41	0.21	0.00	0.70
C2-3W-01	SAMPLE 1	BULK ROCK	52.6	2656.0	1.81	1.81	0.41	67.48	336.60	468.00	0.50	66.00	16.00	1.20	0.32	2.40	2.72	0.52	0.20	0.01	0.79
C2-1M-01	SAMPLE 1	BULK ROCK	51.3	2624.0	1.52	1.90	0.65	74.05	454.53	451.00	0.44	66.00	22.00	0.91	0.31	2.59	2.90	0.25	0.21	0.01	0.53
C2-2M-01	SAMPLE 1	BULK ROCK	52.7	2634.0	1.47	1.74	0.52	77.85	442.33	458.00	0.46	57.00	17.00	1.04	0.29	2.74	3.03	0.31	0.22	0.00	0.58
C2-3M-01	SAMPLE 1	BULK ROCK	52.9	4737.0	2.72	3.13	0.41	72.58	413.39	498.00	0.46	101.00	14.00	1.06	0.50	2.59	3.10	0.39	0.24	0.01	0.69
C2-1M-01	SAMPLE 1	BULK ROCK	50.0	2610.0	1.27	1.57	0.40	60.03	311.55	468.00	0.45	65.00	16.00	1.20	0.25	2.16	2.41	0.31	0.20	0.00	0.56
C2-0H-02	SAMPLE 2	BULK ROCK	52.5	2495.0	2.19	5.09	0.91	68.68	321.35	388.00	0.30	166.00	30.00		0.61	2.43	3.07	0.04	0.23	0.00	0.31
C2-1H-02	SAMPLE 2	BULK ROCK	53.4	2495.0	2.22	3.10	0.39	69.06	353.25	470.00	0.42	104.00	13.00	1.22	0.46	2.53	2.99	0.09	0.27	0.05	0.43
C2-2H-02	SAMPLE 2	BULK ROCK	51.8	2611.0	2.23	3.01	0.38	71.05	356.23	468.00	0.43	99.00	13.00	1.20	0.45	2.58	3.03	0.06	0.24	0.04	0.35
C2-3H-02	SAMPLE 2	BULK ROCK	51.3	2611.0	2.31	3.03	0.42	70.83	347.54	466.00	0.43	100.00	14.00	1.17	0.46	2.57	3.03	0.07	0.21	0.00	0.31
C2-4H-02	SAMPLE 2	BULK ROCK	52.0	2611.0	2.08	3.08	0.43	71.73	352.88	468.00	0.40	102.00	14.00	1.19	0.45	2.58	3.02	0.04	0.24	0.02	0.31
C2-4H-02	SAMPLE 2	BULK ROCK	53.6	2578.0	2.58	3.13	0.49	71.58	351.22	468.00	0.45	102.00	16.00	1.19	0.49	2.58	3.07	0.04	0.19	0.03	0.28
C2-72H-02	SAMPLE 2	BULK ROCK	51.6	2578.0	2.12	2.79	0.39	71.05	353.50	472.00	0.43	94.00	13.00	1.25	0.42	2.56	2.98	0.04	0.20	0.07	0.32
C2-1W-02	SAMPLE 2	BULK ROCK	51.2	2530.0	2.06	2.80	0.38	71.42	348.70	465.00	0.42	94.00	13.00	1.14	0.42	2.56	2.98	0.03	0.24	0.00	0.30
C2-2W-02	SAMPLE 2	BULK ROCK	53.3	2615.0	2.28	2.99	0.41	72.86	355.30	462.00	0.43	97.00	13.00	1.10	0.46	2.62	3.08	0.03	0.22	0.06	0.33
C2-3W-02	SAMPLE 2	BULK ROCK	52.7	2658.0	1.96	2.85	0.41	71.05	341.00	469.00	0.41	96.00	14.00	1.22	0.42	2.54	2.96	0.03	0.21	0.01	0.26
C2-1M-02	SAMPLE 2	BULK ROCK	52.2	2624.0	1.95	2.92	0.36	89.17	465.15	470.00	0.40	80.00	10.00	1.23	0.42	3.22	3.64	0.06	0.41	0.01	0.49
C2-2M-02	SAMPLE 2	BULK ROCK	53.2	2634.0	1.80	3.14	0.52	95.50	433.64	467.00	0.36	81.00	13.00	1.18	0.43	3.43	3.86	0.11	0.38	0.08	0.59
C2-3M-02	SAMPLE 2	BULK ROCK	53.8	4737.0	3.48	5.22	0.45	82.74	424.67	473.00	0.40	141.00	12.00	1.27	0.74	2.96	3.70	0.03	0.31	0.00	0.35
C2-1M-02	SAMPLE 2	BULK ROCK	53.7	2610.0	1.73	2.72	0.46	73.02	352.10	468.00	0.39	91.00	15.00	1.20	0.39	2.61	3.00	0.03	0.20	0.04	0.29
C2-0H-03	SAMPLE 3	BULK ROCK	52.0	2495.0	2.57	3.96	0.61	71.98	330.71	388.00	0.39	123.00	19.00		0.57	2.64	3.21	0.14	0.19	0.05	0.43
C2-1H-03	SAMPLE 3	BULK ROCK	53.1	2495.0	2.53	3.46	0.47	71.97	337.38	468.00	0.42	108.00	15.00	1.19	0.52	2.68	3.19	0.18	0.19	0.06	0.47
C2-2H-03	SAMPLE 3	BULK ROCK	55.2	2611.0	2.38	3.13	0.43	68.81	318.12	468.00	0.43	101.00	14.00	1.19	0.47	2.54	3.01	0.13	0.17	0.11	0.43
C2-3H-03	SAMPLE 3	BULK ROCK	52.5	2611.0	2.42	3.09	0.49	70.20	346.09	464.00	0.44	101.00	16.00	1.13	0.48	2.57	3.05	0.12	0.19	0.01	0.35
C2-4H-03	SAMPLE 3	BULK ROCK	53.6	2611.0	2.06	2.73	0.42	68.51	343.21	466.00	0.43	94.00	15.00	1.16	0.42	2.49	2.91	0.09	0.24	0.01	0.36
C2-4H-03	SAMPLE 3	BULK ROCK	52.2	2578.0	2.10	2.76	0.39	68.20	349.24	474.00	0.43	94.00	13.00	1.29	0.42	2.51	2.93	0.13	0.26	0.05	0.47
C2-72H-03	SAMPLE 3	BULK ROCK	53.0	2578.0	2.24	2.79	0.45	68.69	345.98	474.00	0.45	95.00	15.00	1.23	0.43	2.51	2.95	0.12	0.25	0.02	0.43
C2-1W-03	SAMPLE 3	BULK ROCK	52.6	2530.0	1.93	2.59	0.36	67.98	345.24	466.00	0.43	90.00	12.00	1.16	0.39	2.49	2.88	0.14	0.19	0.09	0.44
C2-2W-03	SAMPLE 3	BULK ROCK	51.3	2615.0	2.12	2.71	0.41	69.09	345.63	463.00	0.41	93.00	14.00	1.11	0.42	2.52	2.94	0.13	0.25	0.02	0.42
C2-3W-03	SAMPLE 3	BULK ROCK	52.0	2658.0	1.90	2.51	0.42	70.21	343.63	468.00	0.43	87.00	14.00	1.20	0.39	2.55	2.93	0.12	0.16	0.03	0.33
C2-1M-03	SAMPLE 3	BULK ROCK	51.7	2624.0	1.77	2.40	0.35	81.87	440.21	467.00	0.43	70.00	10.00	1.17	0.36	3.08	3.44	0.12	0.31	0.01	0.46
C2-2M-03	SAMPLE 3	BULK ROCK	51.3	2634.0	1.73	2.66	0.42	91.82	468.84	470.00	0.39	72.00	11.00	1.22	0.38	3.33	3.72	0.14	0.18	0.19	0.54
C2-3M-03	SAMPLE 3	BULK ROCK	52.5	4737.0	3.98	5.40	0.56	84.28	407.58	469.00	0.42	140.00	14.00	1.21	0.80	3.06	3.86	0.09	0.23	0.02	0.37
C2-1M-03	SAMPLE 3	BULK ROCK	45.0	2610.0	1.91	2.63	0.53	74.09	336.08	463.00	0.42	85.00	17.00	1.12	0.40	2.70	3.10	0.11	0.17	0.01	0.31
C2-0H-04	SAMPLE 4	BULK ROCK	54.1	2495.0	2.28	4.65	0.76	59.39	326.00	388.00	0.33	170.00	28.00		0.61	2.12	2.73	0.03	0.24	0.01	0.29
C2-1H-04	SAMPLE 4	BULK ROCK	50.5	2495.0	2.39	3.38	0.51	60.72	346.13	461.00	0.41	125.00	20.00	1.09	0.50	2.20	2.70	0.03	0.22	0.00	0.26
C2-2H-04	SAMPLE 4	BULK ROCK	52.9	2611.0	2.31	2.94	0.45	63.37	356.69	463.00	0.41	107.00	16.00	1.12	0.45	2.29	2.74	0.02	0.17	0.01	0.21
C2-3H-04	SAMPLE 4	BULK ROCK	53.1	2611.0	2.08	3.23	0.40	61.46	351.37	464.00	0.39	119.00	15.00	1.13	0.46	2.25	2.71	0.04	0.24	0.02	0.31
C2-4H-04	SAMPLE 4	BULK ROCK	50.8	2611.0	2.21	2.80	0.34	60.78	358.76	466.00	0.44	105.00	13.00	1.16	0.43	2.23	2.66	0.05	0.27	0.01	0.33
C2-4H-04	SAMPLE 4	BULK ROCK	51.1	2578.0	2.31	2.83	0.39	62.37	359.85	468.00	0.45	104.00	14.00	1.20	0.44	2.28	2.72	0.04	0.25	0.01	0.30
C2-72H-04	SAMPLE 4	BULK ROCK	54.3	2578.0	2.22	2.95	0.42	61.40	357.06	468.00	0.43	110.00	16.00	1.20	0.45	2.23	2.67	0.03	0.23	0.03	0.30
C2-1W-04	SAMPLE 4	BULK ROCK	51.6	2530.0	2.19	3.01	0.45	62.28	353.57	461.00	0.42	112.00	17.00	1.09	0.45	2.24	2.70	0.02	0.22	0.00	0.25
C2-2W-04	SAMPLE 4	BULK ROCK	52.1	2615.0	2.44	3.22	0.50	64.59	358.13	458.00	0.43	114.00	18.00	1.03	0.49	2.32	2.81	0.02	0.21	0.00	0.24
C2-3W-04	SAMPLE 4	BULK ROCK	52.6	2658.0	2.18	2.90	0.36	63.44	361.90	466.00	0.43	105.00	13.00	1.16	0.44	2.32	2.73	0.03	0.22	0.01	0.28
C2-1M-04	SAMPLE 4	BULK ROCK	51.1	2624.0	1.99	2.87	0.36	76.76	441.60	467.00	0.41	90.00	11.00	1.18	0.42	2.79	3.21	0.01	0.34	0.02	0.41
C2-2M-04	SAMPLE 4	BULK ROCK	51.5	2634.0	1.95	2.61	0.38	81.38	493.49	469.00	0.43	76.00	11.00	1.21	0.40	3.06	3.46	0.03	0.22	0.09	0.36
C2-3M-04	SAMPLE 4	BULK ROCK	52.2	4737.0	3.50	4.66	0.35	73.05	441.33	474.00	0.43	140.00	10.00	1.28	0.69	2.65	3.34	0.02	0.31	0.00	0.34
C2-1M-04	SAMPLE 4	BULK ROCK	51.6	2610.0	1.84	2.57	0.38	65.17	364.55	469.00	0.42	93.00	14.00	1.21	0.38	2.37	2.75	0.02	0.19	0.04	0.26
C2-0H-05	SAMPLE 5	BULK ROCK	52.6	2495.0	2.34	2.93	0.41	68.42	351.19	466.00	0.41	99.00	15.00</								

S1 from the outer core surface that is sampled immediately after unwrapping the core shows 2.25 mgHC/g. This value is close enough to S1 values from the four samples that ranged from 2.09-2.29 mgHC/g (Table 21).

Table 21: S1 data (mgHC/g) comparison between outer core surface and the four core samples at 0h (fresh samples) from Core 2.

Time	Outer Surface	Sample 1	Sample 2	Sample 3	Sample 4
0h	2.25	2.09	2.25	2.29	2.31

In Core 2, S1 results show minor changes over time. The four samples show identical trends in the four samples (Table 22 & Figure 10).

Table 22: S1 data (mgHC/g) difference in Core 2 between the first three runs fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 3 months, and after 4 months (3MN and 4MN) for the four samples.

Sample ID	Avg (0h,1h and 2h)	Avg (3MN and 4MN)	Δ S1 (mg/g)	Δ %
Sample 1	2.3	2.0	0.3	14.6
Sample 2	2.2	2.6	-0.4	-17.7
Sample 3	2.5	2.9	-0.5	-18.1
Sample 4	2.3	2.7	-0.3	-14.8

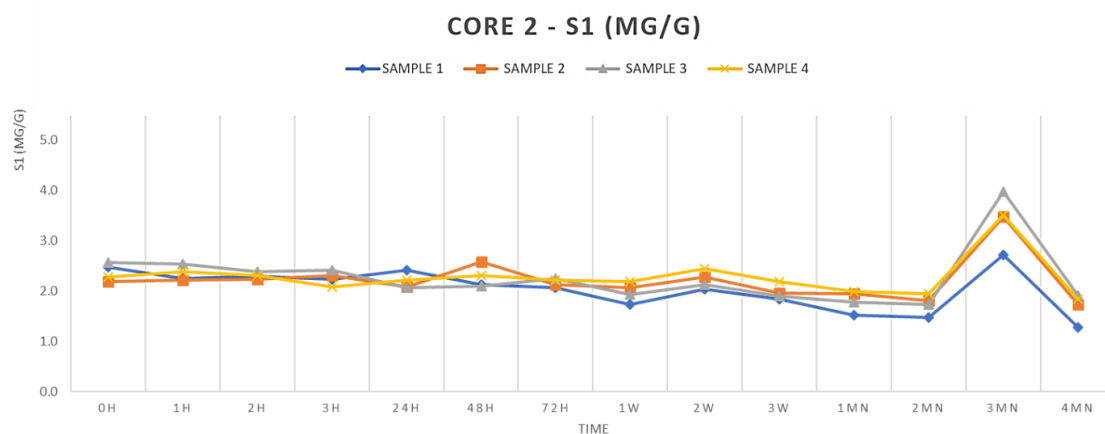


Figure 10: S1 (mgHC/g) change with time for the four samples from Core 2. This core is tested for up to 4 month-time cycles. The increase in S1 (light hydrocarbons) reflected by the high peaks of the different samples in the 3 months run (3MN) indicate the impact of the change of the sampling position, which also reflects the lateral heterogeneity in the laminae at the micro-scale.

To ensure data quality, similar to Core1. Duplicated samples are tested from Sample 2,—those samples labeled as Sample 5. The S1 values for both samples (Sample 2 and Sample 5) show a maximum difference of 0.18 mgHC/g. (Table 23).

Table 23: S1 data (mgHC/g) quality check test (QC). Sample 2 and Sample 5 results from Core 2.

QC Test - S1 (mg/g)				
Sample ID	0h	3h	3W	4MN
Sample 2	2.19	2.31	1.96	1.73
Sample 5	2.34	2.13	1.90	1.71
Δ S1 (mg/g)	-0.15	0.18	0.06	0.02
Δ %	106.8	92.2	96.9	98.8

For S2 values, S2 from the outer core surface that is sampled immediately after unwrapping the core shows 9.10 mgHC/g. This value is way off compared with the other four samples from the same core. S2 values for the other four samples range between 2.39-3.32 mgHC/g (Table 24)

Table 24: S2 data (mgHC/g) comparison between outer core surface and the four core samples at 0h (fresh samples) from Core 2.

Time	Outer Surface	Sample 1	Sample 2	Sample 3	Sample 4
0h	9.10	2.39	3.32	3.10	3.24

The S2 behavior is almost identical through the four samples in Core 2. S2 starts to decrease slightly after 1 hour (Table 25). Overall, no significant changes were exhibited in S2 values over time in Core 2 (Figure 11).

Table 25: S2 data (mgHC/g) difference in Core 2 between the first three runs of fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 3 months, and after 4 months (3MN and 4MN) for the four samples.

Sample ID	Avg (0h,1h and 2h)	Avg (3MN and 4MN)	Δ S2 (mg/g)	Δ %
Sample 1	3.23	2.35	0.88	27.2
Sample 2	3.73	3.97	-0.24	-6.3
Sample 3	3.52	4.02	-0.50	-14.2
Sample 4	3.66	3.62	0.04	1.1

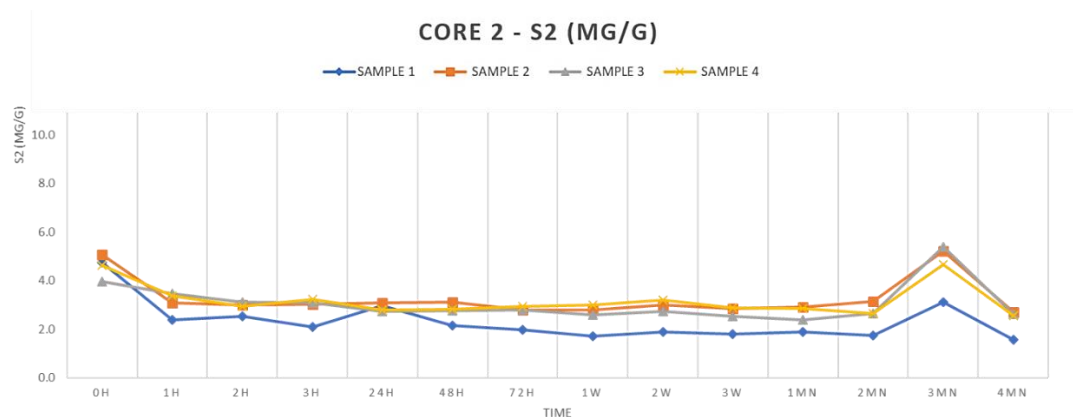


Figure 11: S2 (mgHC/g) changes over time for the four samples from Core 2. This core is tested up to 4 months-time cycles. The increase in S2 value reflected by the high peaks of the different samples in the 3 months (3MN) indicate the impact of the change of the sampling position, which also reflects the lateral heterogeneity in the laminae at the micro-scale.

Similar to core 1, duplicate samples are tested. The S2 values for both samples (Sample 2 and Sample 5) show an accepted difference that is ranged from 0.05-2.16 mgHC/g. (Table 26)

Table 26: S2 data (mgHC/g) quality check test (QC). Sample 2 and Sample5 results from Core 2

Sample ID	QC Test - S2 (mg/g)			
	0h	3h	3W	4MN
Sample 2	5.09	3.03	2.85	2.72
Sample 5	2.93	2.92	2.72	2.67
Δ S2 (mg/g)	2.16	0.11	0.13	0.05
Δ %	57.6	96.4	95.4	98.2

The T_{MAX} from Core 2 shows more pronounced fluctuation with time. T_{MAX} from the outer core surface shows 380°C. This value is a way off compared with the other four samples. T_{MAX} values for Sample 1 is 413°C. However, the other three samples are relatively higher and range from 459.5-462.0°C (Table 27).

Table 27: T_{MAX} data (°C) comparison between outer core surface and the four core samples at 0h (fresh samples) in Core 2

Time	Outer Surface	Sample 1	Sample 2	Sample 3	Sample 4
0h	380	413	462	462	459

Overall, the T_{MAX} trend shows no significant changes over storage time. An increase after the first run (0h) followed by almost negligible changes except for Sample 1. Sample 1 shows relatively lower T_{MAX} values across time until 3 weeks run (3W). Results from a 3-week test show comparable values from Sample 1 to the other three samples (Table 28 and Figure 12).

Table 28: T_{MAX} data ($^{\circ}\text{C}$) difference in Core 2 between the first three runs fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 3 months, and after 4 months (3MN and 4MN) for the four samples.

Sample ID	Avg (0h,1h and 2h)	Avg (3MN and 4MN)	ΔT_{max} ($^{\circ}\text{C}$)	$\Delta \%$
Sample 1	384	464	-80	-20.7
Sample 2	442	471	-29	-6.4
Sample 3	441	466	-25	-5.6
Sample 4	437	472	-34	-7.8

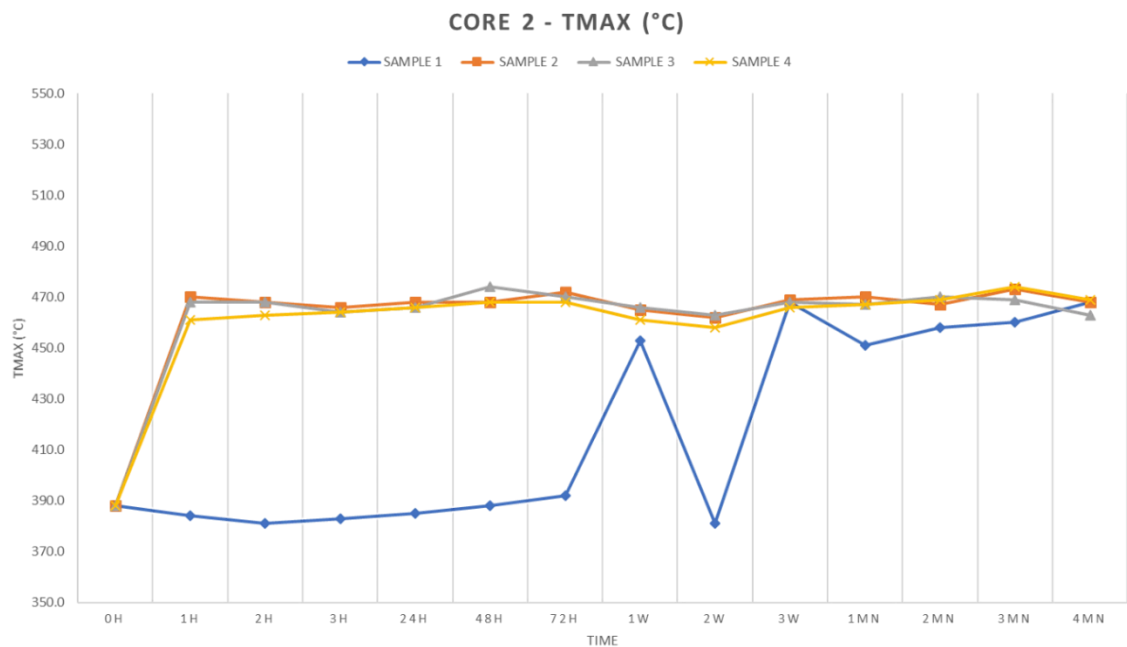


Figure 12: T_{MAX} ($^{\circ}\text{C}$) change with time for the four samples from Core 2. This core is tested for up to 4 months-time cycles. Sample1values has demonstrated that organic additives to drilling mud can be detected on pyrolysis measurements through T_{MAX} . With increased time, the sample that was taken from deeper intervals during the four-month run (4MN) proved that sample was mitigated and avoided any contaminants from drilling and the outer surface with comparable value compare with the other three samples.

Similar to the other tests, the duplicated samples (Sample 2 and Sample 5) are comparable with a difference in T_{MAX} range from $\Delta 1$ - 3°C for three tests (3h, 3W & 4 MN). While the first test during the 0h run was an outlier with a difference of $\Delta 78^{\circ}\text{C}$ (Table 29).

Table 29 T_{MAX} data ($^{\circ}\text{C}$) quality check test (QC). Sample 2 and Sample 5 results from Core 2.

Sample ID	QC Test -Tmax ($^{\circ}\text{C}$)			
	0h	3h	3W	4MN
Sample 2	388	466	469	468
Sample 5	466	467	472	467
ΔT_{max} ($^{\circ}\text{C}$)	-78	-1	-3	1
$\Delta \%$	120	100	101	100

Finally, TOC measurements from Core 2 show no significant change with time. TOC from the outer core surface shows 3.17% TOC. This value is close to the other four samples from the same core that ranged from 2.75-3.19% TOC (Table 30).

Table 30: TOC data (%) comparison between outer core surface and the four core samples at 0h (fresh samples) in Core 2

Time	Outer Surface	Sample 1	Sample 2	Sample 3	Sample 4
0h	3.17	2.75	3.19	3.16	2.86

Overall, TOC measurements from the four samples are within a narrow range. The TOC behavior through the different time cycles up to 4 months is almost identical in the four samples. (Table 31 & Figure 13).

Table 31: TOC data (%) difference in Core 2 between the first three runs fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 3 months, and after 4 months (3MN and 4MN) for the four samples.

Sample ID	Avg (0h,1h and 2h)	Avg (3MN and 4MN)	ΔTOC (%)	$\Delta \%$
Sample 1	2.80	2.76	0.05	1.7
Sample 2	3.03	3.35	-0.32	-10.6
Sample 3	3.14	3.48	-0.34	-10.9
Sample 4	2.72	3.05	-0.32	-11.8

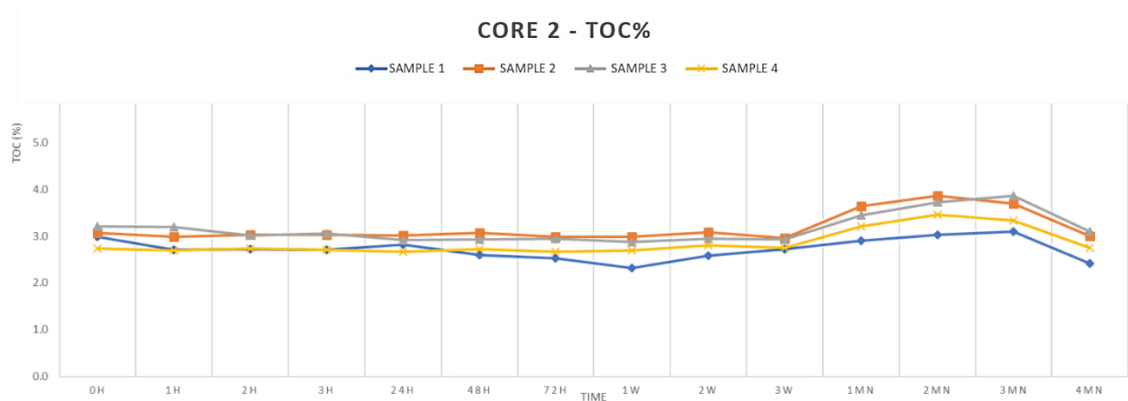


Figure 13: TOC (%) change with time for the four samples from Core 2. This core is tested up to 4 months-time cycles. The increase in TOC values reflected by the high peaks of the different samples in the 1 month, 2 months and 3 months runs (1MN, 2MN & 3MN) indicate the impact of the change of the sampling position, which also reflects the lateral heterogeneity in the laminae at the micro-scale.

For the duplicate samples (Sample 2 and Sample 5). Results also show minor differences in three test runs. The values are within the TOC normal fluctuation (Table 32).

Table 32: TOC data (%) quality check test (QC). Sample 2 and Sample 5 results from Core 2.

QC Test -TOC %			
Sample ID	0h	3h	3W
Sample 2	3.07	3.03	2.96
Sample 5	2.94	3.00	2.96
Δ TOC (%)	0.13	0.03	0.00
Δ %	95.8	99.0	100.0

4.2.3 Pyrolysis Results from Core 3

On October, 23rd (2022), Core 3 was opened for the first lab run. 21 samples were collected from this core on the first day for the assigned lab runs (Figure 2). Overall, 62 samples in total are used from Core 3 (Table 33). This core was tested over 4 months and was exposed (unpreserved) for 121 days under normal conditions. The core is kept in a closed store with gradually decreasing weather temperatures that are ranged from 37°C to 12°C (outside temperature) and with an average store temperature of 19°C (Figure 14).

Figure 14: Core 3 storing temperature forecast. The average store temperature is 19°C and the outside temperature is 25°C

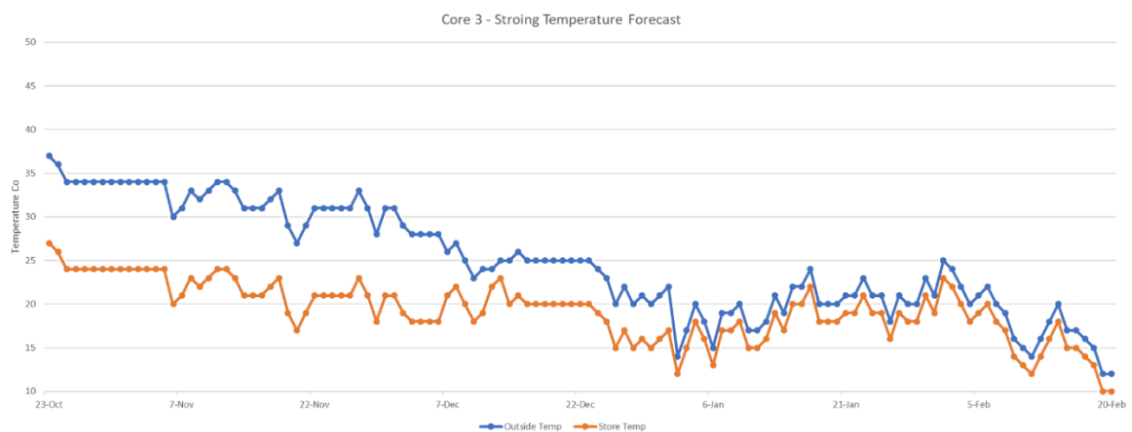


Table 33: Core 3 pyrolysis results.

Analysis	Sample	Method	Quantity (mg)	KfId	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	S4CO2 (mg/g)	S5 (mg/g)	Temp (°C)	PI	HI	OI	Estimated Ro	PC (%)	RC (%)	TOC (%)	Residual S (%)	Retained S (%)	Sulfate S (%)	Total S (%)
C3-SURF-01	Surf_Sample1	BULK ROCK	52.2	2608.0	2.08	7.31	1.57	112.01	267.54	402.00	0.22	173.00	37.00		0.85	3.38	4.23	0.00	0.06	0.00	0.32
C3-SURF-03	Surf_Sample3	BULK ROCK	52.5	2608.0	2.58	7.35	1.31	105.45	311.94	408.00	0.26	174.00	31.00		0.89	3.34	4.22	0.00	0.11	0.01	0.33
C3-SURF-02	Surf_Sample2	BULK ROCK	52.7	2608.0	3.40	10.64	1.70	172.44	226.68	443.00	0.24	154.00	25.00	0.76	1.25	5.66	6.90	0.00	0.07	0.00	0.31
C3-SURF-01	Surf_Sample1	BULK ROCK	53.9	2608.0	1.58	8.06	1.68	73.59	270.92	404.00	0.16	252.00	53.00		0.88	2.32	3.20	0.00	0.07	0.01	0.33
C3-SURF-ALL	Surface_All	BULK ROCK	53.3	2608.0	1.97	7.57	1.58	82.93	239.40	400.00	0.21	220.00	46.00		0.87	2.58	3.45	0.00	0.07	0.00	0.28
C3-0H-01	Sample1	BULK ROCK	54.4	2608.0	1.49	2.87	0.66	62.25	372.12	415.00	0.34	110.00	26.00	0.81	0.39	2.21	2.60	0.04	0.22	0.01	0.32
C3-1H-01	Sample1	BULK ROCK	54.5	2608.0	1.64	2.73	0.50	59.85	375.89	451.00	0.38	109.00	20.00	0.91	0.38	2.11	2.50	0.03	0.17	0.05	0.37
C3-2H-01	Sample1	BULK ROCK	50.6	2604.0	1.71	2.67	0.51	60.56	376.89	454.00	0.39	107.00	20.00	0.97	0.39	2.12	2.50	0.02	0.18	0.01	0.29
C3-3H-01	Sample1	BULK ROCK	51.5	2604.0	1.66	2.97	0.56	63.42	372.79	457.00	0.36	112.00	21.00	1.01	0.41	2.24	2.65	0.02	0.19	0.03	0.37
C3-2H-01	Sample1	BULK ROCK	52.8	2604.0	1.67	2.97	0.58	65.23	373.74	456.00	0.36	112.00	22.00	1.00	0.41	2.24	2.65	0.01	0.14	0.09	0.36
C3-4H-01	Sample1	BULK ROCK	53.0	2624.0	1.80	3.07	0.54	83.37	514.69	452.00	0.37	93.00	16.00	0.93	0.43	2.88	3.31	0.02	0.31	0.01	0.37
C3-72H-01	Sample1																				
C3-1W-01	Sample1	BULK ROCK	54.1	2624.0	1.49	2.81	0.69	66.98	440.27	449.00	0.35	105.00	26.00	0.87	0.39	2.30	2.69	0.01	0.21	0.01	0.28
C3-2W-01	Sample1	BULK ROCK	36.0	2565.0	1.52	2.65	0.54	66.62	421.66	452.00	0.37	99.00	20.00	0.92	0.37	2.30	2.67	0.00	0.00	0.00	0.09
C3-3W-01	Sample1	BULK ROCK	51.3	2569.0	1.61	2.74	0.50	70.33	463.17	458.00	0.37	96.00	18.00	1.03	0.38	2.46	2.81	0.01	0.20	0.03	0.29
C3-1MN-01	Sample1	BULK ROCK	50.8	2634.0	1.52	2.72	0.50	71.84	490.93	458.00	0.36	94.00	17.00	1.04	0.37	2.52	2.89	0.01	0.25	0.07	0.39
C3-2MN-01	Sample1	BULK ROCK	52.5	4737.0	3.16	5.64	0.42	71.25	455.65	460.00	0.36	173.00	13.00	1.06	0.75	2.51	3.26	0.02	0.23	0.03	0.31
C3-3MN-01	C3-3MN-01	BULK ROCK	48.4	2580.0	1.38	2.65	0.41	57.46	373.46	458.00	0.34	111.00	17.00	1.03	0.35	2.03	2.39	0.01	0.17	0.04	0.25
C2-1MN-01	C2-1MN-01	BULK ROCK	58.0	2610.0	1.27	1.57	0.40	60.03	341.53	466.00	0.45	65.00	16.00	1.28	0.25	2.16	2.41	0.31	0.20	0.00	0.56
C3-0H-02	Sample2	BULK ROCK	53.3	2608.0	3.59	6.39	0.83	107.43	346.62	451.00	0.36	137.00	18.00	0.91	0.87	3.79	4.66	0.01	0.20	0.04	0.41
C3-1H-02	Sample2	BULK ROCK	52.5	2608.0	3.42	5.83	0.63	103.53	348.50	456.00	0.37	130.00	14.00	0.99	0.80	3.70	4.50	0.01	0.18	0.07	0.38
C3-2H-02	Sample2	BULK ROCK	53.1	2604.0	3.55	6.52	0.56	105.90	348.80	464.00	0.35	137.00	12.00	1.13	0.86	3.91	4.78	0.01	0.23	0.02	0.36
C3-3H-02	Sample2	BULK ROCK	52.7	2601.0	3.33	5.91	0.55	102.32	347.07	463.00	0.36	133.00	12.00	1.12	0.79	3.66	4.45	0.01	0.22	0.00	0.31
C3-3H-02	Sample2	BULK ROCK	51.3	2601.0	3.36	6.00	0.74	108.86	343.30	460.00	0.36	132.00	16.00	1.06	0.81	3.74	4.55	0.01	0.20	0.01	0.31
C3-4H-02	Sample2	BULK ROCK	50.8	2624.0	3.34	5.77	0.47	135.78	484.03	458.00	0.37	102.00	8.00	1.03	0.78	4.88	5.65	0.01	0.33	0.01	0.40
C3-72H-02	Sample2																				
C3-1W-02	Sample2	BULK ROCK	51.8	2624.0	3.25	6.18	0.77	156.45	482.60	455.00	0.34	99.00	12.00	0.99	0.82	5.44	6.25	0.00	0.22	0.00	0.30
C3-2W-02	Sample2	BULK ROCK	41.3	2565.0	3.23	5.61	0.55	114.89	403.34	458.00	0.37	116.00	11.00	1.03	0.76	4.09	4.85	0.00	0.00	0.00	0.03
C3-3W-02	Sample2	BULK ROCK	43.7	2589.0	3.05	5.54	0.44	121.43	432.18	463.00	0.36	109.00	9.00	1.12	0.73	4.34	5.07	0.01	0.23	0.00	0.31
C3-1MN-02	Sample2	BULK ROCK	52.8	2634.0	2.98	5.86	0.54	131.46	451.78	462.00	0.34	108.00	10.00	1.10	0.76	4.66	5.42	0.00	0.24	0.06	0.34
C3-2MN-02	Sample2	BULK ROCK	51.6	4737.0	5.51	10.56	0.46	118.39	423.05	465.00	0.34	187.00	8.00	1.15	1.36	4.27	5.63	0.01	0.20	0.11	0.35
C3-3MN-02	C3-3MN-02	BULK ROCK	52.6	2580.0	2.86	6.07	0.42	106.77	350.79	464.00	0.32	129.00	9.00	1.13	0.76	3.93	4.69	0.01	0.25	0.04	0.33
C2-1MN-02	C2-1MN-02	BULK ROCK	53.7	2610.0	1.73	2.72	0.46	73.02	352.10	466.00	0.39	91.00	15.00	1.28	0.39	2.61	3.00	0.03	0.20	0.01	0.29
C3-0H-03	Sample3	BULK ROCK	53.7	2608.0	3.02	5.59	0.70	104.97	354.18	453.00	0.35	124.00	15.00	0.95	0.75	3.78	4.52	0.04	0.16	0.03	0.41
C3-1H-03	Sample3	BULK ROCK	52.8	2608.0	3.18	5.80	0.58	108.04	358.41	456.00	0.35	123.00	12.00	1.00	0.77	3.95	4.72	0.05	0.17	0.01	0.37
C3-2H-03	Sample3	BULK ROCK	51.5	2604.0	2.94	5.40	0.50	103.34	357.18	463.00	0.35	120.00	11.00	1.11	0.72	3.77	4.49	0.05	0.17	0.00	0.32
C3-3H-03	Sample3	BULK ROCK	52.5	2604.0	2.78	5.09	0.47	97.01	351.59	464.00	0.35	121.00	11.00	1.13	0.67	3.54	4.21	0.05	0.17	0.00	0.30
C3-2H-03	Sample3	BULK ROCK	52.8	2604.0	2.83	4.82	0.47	92.34	360.15	460.00	0.37	120.00	12.00	1.07	0.66	3.35	4.00	0.03	0.18	0.03	0.32
C3-4H-03	Sample3	BULK ROCK	52.9	2624.0	2.94	5.40	0.48	136.75	500.20	460.00	0.35	95.00	9.00	1.06	0.71	4.95	5.67	0.05	0.23	0.00	0.35
C3-72H-03	Sample3																				
C3-1W-03	Sample3	BULK ROCK	52.0	2624.0	2.72	5.25	0.62	129.42	468.59	458.00	0.34	100.00	12.00	1.02	0.69	4.58	5.27	0.02	0.15	0.02	0.25
C3-2W-03	Sample3	BULK ROCK	42.5	2565.0	2.58	4.88	0.41	110.41	436.07	459.00	0.35	105.00	9.00	1.04	0.61	4.01	4.65	0.16	0.00	0.00	0.23
C3-3W-03	Sample3	BULK ROCK	51.3	2569.0	2.38	4.65	0.45	118.54	481.73	462.00	0.34	95.00	9.00	1.09	0.61	4.28	4.89	0.03	0.22	0.02	0.33
C3-1MN-03	Sample3	BULK ROCK	52.3	2634.0	2.61	5.29	0.50	129.04	472.10	462.00	0.33	99.00	9.00	1.09	0.68	4.65	5.33	0.03	0.26	0.00	0.36
C3-2MN-03	Sample3	BULK ROCK	51.4	4737.0	4.54	9.08	0.41	110.52	436.96	465.00	0.33	176.00	8.00	1.15	1.15	4.00	5.15	0.03	0.21	0.06	0.37
C3-3MN-03	C3-3MN-03	BULK ROCK	47.3	2580.0	2.36	4.60	0.45	97.16	346.44	463.00	0.34	110.00	11.00	1.12	0.60	3.59	4.18	0.24	0.19	0.01	0.49
C2-4MN-03	C2-4MN-03	BULK ROCK	43.0	2610.0	1.91	2.63	0.53	74.09	336.08	463.00	0.42	85.00	17.00	1.12	0.40	2.70	3.10	0.11	0.17	0.01	0.31
C3-0H-04	Sample4	BULK ROCK	53.6	2608.0	2.43	4.90	0.72	92.09	357.29	450.00	0.33	125.00	18.00	0.89	0.64	3.27	3.91	0.02	0.19	0.01	0.48
C3-1H-04	Sample4	BULK ROCK	52.6	2608.0	2.43	4.43	0.56	93.43	363.73	453.00	0.35	113.00	14.00	0.95	0.59	3.33	3.93	0.03	0.20	0.00	0.47
C3-2H-04	Sample4	BULK ROCK	53.4	2604.0	2.32	4.43	0.52	90.99	353.74	460.00	0.34	115.00	14.00	1.06	0.58	3.26	3.84	0.03	0.18	0.02	0.45
C3-3H-04	Sample4	BULK ROCK	54.6	2604.0	2.33	4.62	0.51	90.27	355.84	460.00	0.34	120.00	13.00	1.07	0.60	3.24	3.84	0.03	0.18	0.03	0.40
C3-24H-04	Sample4	BULK ROCK	52.3	2604.0	2.56	4.37	0.50	89.23	355.56	459.00	0.35	116.00	12.00	1.05	0.58	3.19	3.77	0.03	0.20	0.02	0.44
C3-4H-04	Sample4	BULK ROCK	51.7	2624.0	2.38	4.55	0.59	123.41	488.07	454.00	0.34	92.00	12.00	0.96	0.60	4.37	4.97	0.02	0.26	0.01	0.45
C3-72H-04	Sample4																				
C3-1W-04	Sample4	BULK ROCK	50.2	2624.0	2.43	4.64	0.59	114.12	461.57	451.00	0.34	100.00	13.00	0.96	0.61	4.02	4.64	0.01	0.21	0.00	0.35
C3-2W-04	Sample4	BULK ROCK	41.3	2565.0	2.27	4.65	0.68	110.24	416.27	453.00	0.33	105.00	15.00	0.94	0.60	3.85	4.45	0.01	0.16	0.00	0.36
C3-3W-04	Sample4	BULK ROCK	51.6	2569.0	2.37	4.68	0.48	120.82	484.34	458.00	0.34	95.00	10.00	1.03	0.61	4.33	4.94	0.03	0.30	0.00	0.47
C3-1MN-04	Sample4	BULK ROCK	52.4	2634.0	2.54	5.02	0.57	124.84	484.59	459.00	0.34	99.00	11.00	1.05	0.65	4.39	5.05	0.01	0.23	0.02	0.37
C3-2MN-04	Sample4	BULK ROCK	53.6	4737.0	4.57	8.57	0.46	108.14	434.60	461.00	0.34	174.00	9.00	1.09	1.10	3.84	4.94	0.03	0.27	0.01	0.40
C3-3MN-04	C3-																				

Core 3 results show no significant change in S1 values over 2 months. Unlike the other two cores, five samples in total from the outer surface are taken from the exact four sample locations in addition to the representative sample that represents the entire core surface. S1 from the outer core surface that is sampled immediately after unwrapping the core (5 samples in total) shows close S1 values. Those values range from 1.58-3.40 mgHC/g. Furthermore, those surface samples are also within the range of the S1 values from the sample that is taken from fresh deep interior samples from the same core (0h). the reported difference is ranged from 0.1-0.5 mgHC/g (Table 34).

Table 34: S1 data (mgHC/g) comparison between outer core surface samples and deep/interior samples from Core 3 at 0h (fresh samples).

Time	Entire Core	Sample 1	Sample 2	Sample 3	Sample 4
Surface	1.97	1.58	3.40	2.58	2.08
Interior		1.72	3.46	2.91	2.55
Δ S1 (mg/g)		0.14	0.06	0.33	0.47

Generally, a minor change in S1 values is observed over time from this core. The four samples follow similar change trends over time. However, during the two-month run, a slight increase is reported in the S1 values from the four samples (Table 35 and Figure 15).

Table 35: S1 data (mgHC/g) difference in Core 3 between the first three runs fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 3 months, and after 4 months (3MN and 4MN) for the four samples.

Sample ID	Avg (0h, 1h and 2h)	Avg (3MN and 4MN)	Δ S1 (mg/g)	Δ %
Sample 1	1.61	1.33	0.29	17.9
Sample 2	3.52	2.30	1.23	34.8
Sample 3	3.05	2.14	0.91	29.9
Sample 4	2.39	2.13	0.27	11.2

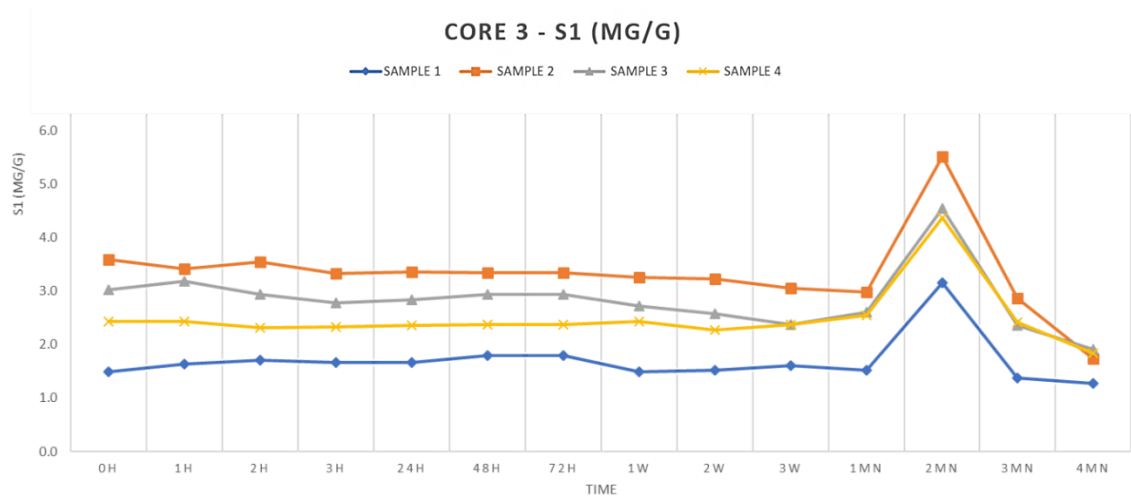


Figure 15: S1 (mgHC/g) change over time for the four samples from Core 3. This core is tested for up to 4 months-time cycles. The increase in S1 (light hydrocarbons) reflected by the high peaks of the different samples in the 2 months run (2MN) indicates the impact of the change of the sampling positions (from surface to center of core) on the pyrolysis results), which also reflects the lateral heterogeneity in the laminae at the micro-scale.

Like the other cores, to ensure data quality, duplicated samples are tested from Sample 2 again. Those samples are tested during 24h run (24h), a 1-week run (1W), a 2-week run (2W), 2 months run (2MN), and after 4 months (4MN). The S1 values for both samples (Sample 2 and Sample 5) are within the accepted range of S1 fluctuation (Table 36).

Table 36: S1 data (mgHC/g) quality check test (QC). Sample 2 and Sample 5 results from Core 3.

Sample ID	QC Test - S1 (mg/g)				
	24h	1W	2W	2MN	4MN
Sample 2	3.36	3.25	3.23	5.51	1.73
Sample 5	3.36	3.18	3.10	5.23	1.71
Δ S1 (mg/g)	0.00	0.07	0.13	0.28	0.02
Δ %	100.0	97.8	96.0	94.9	98.8

For S2 values; S2 from the outer core surface that was sampled immediately after unwrapping the core shows 7.57 mgHC/g. This value is comparable with the other four surface samples. The S2 values for the four samples range from 7.31-10.64 mgHC/g. On the other hand, the interior/deep samples are way off compared with the outer surface samples from the same core. The differences between the two sources (outer and interior) from the four samples range from 1.86-5.02 mgHC/g. (Table 37).

Table 37: S2 data (mgHC/g) comparison between outer core surface and the four core samples at 0h (fresh samples) in Core 3.

Time	Entire Core	Sample 1	Sample 2	Sample 3	Sample 4
Surface	7.57	8.06	10.64	7.35	7.31
Interior		3.04	6.35	5.49	4.98
Δ S2 (mg/g)		-5.02	-4.29	-1.86	-2.34

S2 behavior is almost identical in the four samples. The four samples show minor changes over time. The average difference between the first three runs and the last two runs ranged from 0.65-1.98 mgHC/g (Table 38 and Figure 16).

Table 38: S2 data (mgHC/g) difference in Core 3 between the first three runs fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 3 months, and after 4 months (3MN and 4MN) for the four samples.

Sample ID	Avg (0h, 1h and 2h)	Avg (3MN & 4MN)	Δ S2 (mg/g)	Δ %
Sample 1	2.76	2.11	0.65	23.5
Sample 2	6.25	4.40	1.85	29.6
Sample 3	5.60	3.62	1.98	35.4
Sample 4	4.59	3.71	0.88	19.2

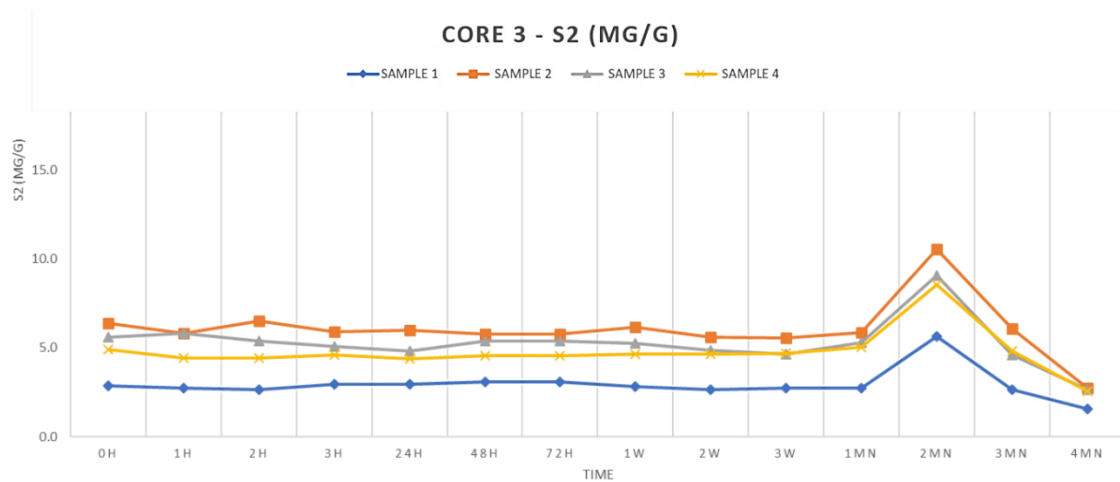


Figure 16: S2 (mgHC/g) changes over time for the four samples from Core 3. The core is tested for up to 4 months-time cycles. The increase in S2 value reflected by the high peaks of the different samples in the 2 months run (2MN) indicate the impact of the change of the sampling position, which also reflects the lateral heterogeneity in the laminae at the micro-scale.

Duplicated samples are tested from Sample 2. Those samples are labeled as Sample 5. The S2 values for both samples (Sample 2 and Sample 5) are within the accepted range of S2 fluctuation (Table 39)

Table 39: S2 data (mgHC/g) quality check test (QC). Sample 2 and Sample 5 results from Core 3

Sample ID	QC Test - S2 (mg/g)				
	24h	1W	2W	2MN	4MN
Sample 2	6.00	6.18	5.61	10.56	2.72
Sample 5	6.00	5.66	4.89	10.52	2.67
Δ S2 (mg/g)	0.00	0.52	0.72	0.04	0.05
Δ %	100.0	91.6	87.2	99.6	98.2

For the T_{MAX} parameter; T_{MAX} from the outer core surface shows a value of 400°C. This value is close to the results from the outer surfaces of Sample 1, Sample 3 and Sample 4. However, Sample 2 is slightly higher with a value of 443°C. However, results from the deep interior samples are higher than the surface results. Adding to this, the average difference between outer samples and interior fresh samples is 52 °C for

Sample 1, Sample 3, and Sample 4, while the difference in Sample 2 is 16.5 °C (Table 40).

Table 40: T_{MAX} data (°C) comparison between the outer core surface and the four core samples at 0h (fresh samples collected at different times and sampling positions) from Core 3.

Time	Entire Core	Sample 1	Sample 2	Sample 3	Sample 4
Surface	400	404	443	408	402
Interior		454	460	460	457
ΔT_{max} (°C)		50	17	52	55

T_{MAX} behavior was almost identical in the four samples. Results after one hour, and after two hours report a slight increase followed by a consistent fluctuation over time until another slight increase after two months (Table 41 and Figure 17).

Table 41: T_{MAX} data (°C) difference in Core between the first three runs of fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 3 months, and after 4 months (3MN and 4MN) for the four samples.

Sample ID	Avg (0h, 1h and 2h)	Avg (3MN and 4MN)	ΔT_{MAX} (°C)	$\Delta \%$
Sample 1	450	463	-13	-3
Sample 2	457	466	-9	-2
Sample 3	457	463	-6	-1
Sample 4	454	466	-11	-2

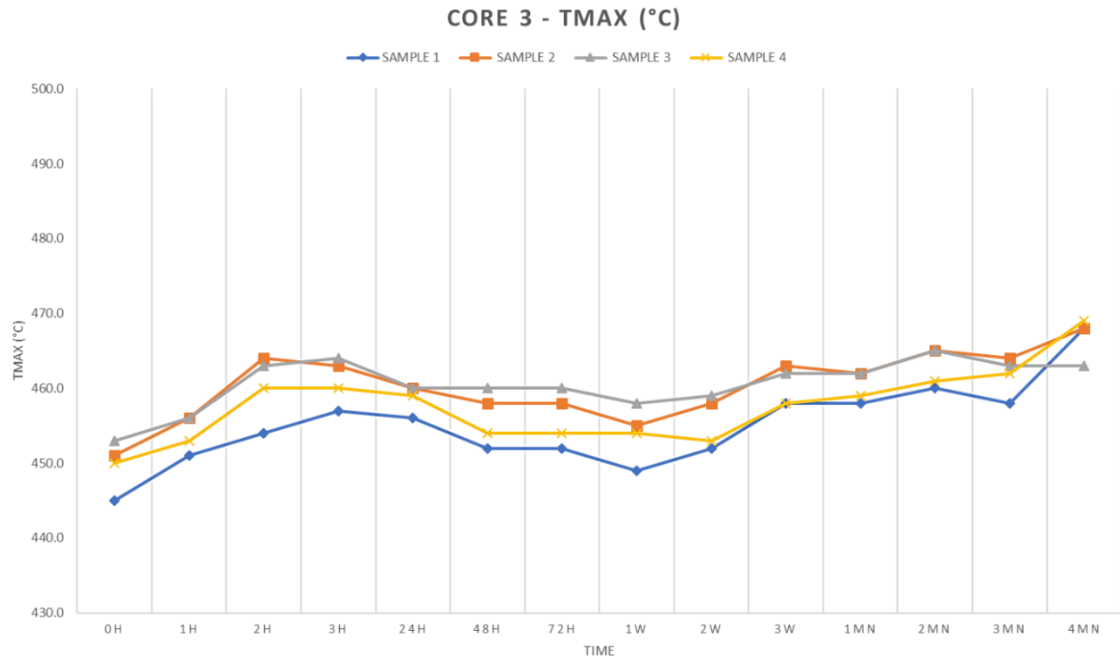


Figure 17: T_{MAX} (°C) changes over time for the four samples from Core 3. The core is tested for up to 4 months-time cycles.

The duplicated samples are performed during 24h (24h), 1 week (1W), 2 weeks (2W), 2 months (2MN), and after 4 months (4MN). Sample 2 and Sample 5 show comparable results within an accepted range of T_{MAX} change ($\Delta 0-4^{\circ}\text{C}$) (Table 42).

Table 42: T_{MAX} data (°C) QC test. Sample 2 and Sample 5 results from Core 3.

Sample ID	QC Test - T_{MAX} (°C)				
	24h	1W	2W	2MN	4MN
Sample 2	460	455	458	465	468
Sample 5	464	457	458	468	467
ΔT_{max} (°C)	-4	-2	0	-3	1
$\Delta \%$	101	100	100	101	100

Finally, TOC measurements from the outer core surface show 3.45% TOC. This value comes close to Sample 1, Sample 3, and Sample 4. While Sample 2 is relatively high with 6.90%.

Furthermore, fresh interior results were also tested from the same four locations. Results show comparable results that range from 2.75-5.04% TOC (Table 43).

Table 43: TOC data (%) comparison between the outer core surface and the four core samples at 0h (fresh samples) in Core 3.

Time	Entire Core	Sample 1	Sample 2	Sample 3	Sample 4
Surface	3.45	3.20	6.90	4.22	4.23
Interior		2.75	5.04	4.76	4.37
Δ TOC (%)		-0.45	-1.86	0.54	0.14

Overall, TOC measurements show minor changes for the four samples from Core 3. The TOC behavior over the different time cycles of up to 5 months is almost identical in the four samples. The four samples show a very minor increase in the TOC values. The difference between the average of the first three runs and the last two runs ranged from 0.13-0.94% TOC. (Table 44 and Figure 18).

Table 44: TOC data (%) difference in Core 3 between the first three runs fresh samples, after 1 hour, and after 2 hours (0h, 1h and 2h) and the last two runs: after 3 months, and after 4 months (3MN and 4MN) for the four samples.

Sample ID	Avg (0h, 1h and 2h)	Avg (3MN and 4MN)	Δ TOC (%)	Δ %
Sample 1	2.53	2.40	0.13	5.3
Sample 2	4.65	3.85	0.80	17.3
Sample 3	4.58	3.64	0.94	20.5
Sample 4	3.89	3.43	0.46	11.9

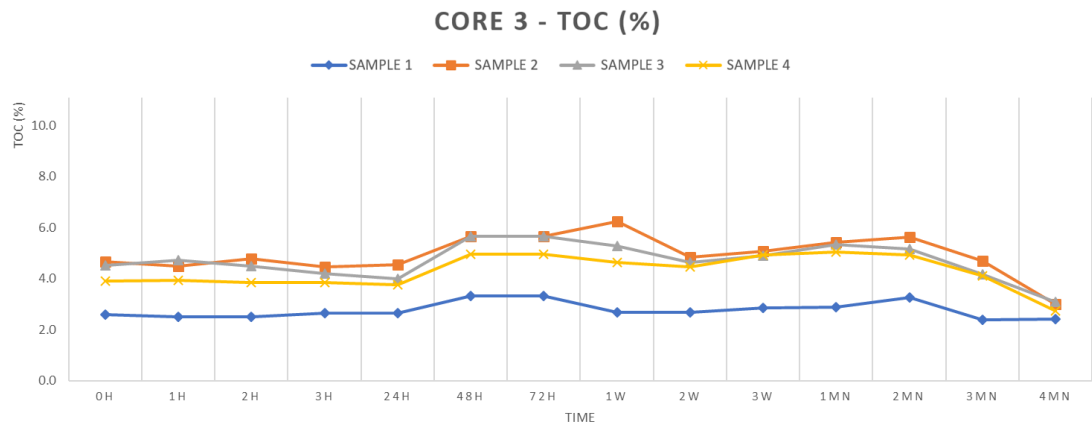


Figure 18: TOC (%) changes over time for the four samples from Core 3. Note the slight fluctuations in the TOC values for each sample with time, indicating the lateral changes in a single bed/lamina and/or change in sampling location (when samples are drilled deeper in the core the TOC value slightly changes). The core is tested for up to 4 month-time cycles.

For the quality control test, Sample 2 and Sample 5 are duplicated. Results show no significant differences between the two samples with a TOC difference that doesn't exceed 1.0% TOC during the different time cycle tests. (Table 45).

Table 45: TOC data (%) QC test results for Sample 2 and 5 from Core 3.

Sample ID	QC Test - TOC (%)				
	24h	1W	2W	2MN	4MN
Sample 2	4.55	6.25	4.85	5.63	3.00
Sample 5	4.49	5.27	4.74	5.58	3.06
Δ TOC (%)	0.06	0.98	0.11	0.05	-0.06
Δ %	98.7	84.3	97.7	99.1	102.0

Chapter 5

Interpretations and Discussion

5.1 Data Quality

Results for standards and results from quality control tests from the three studied cores support the reliability of pyrolysis measurements using the Rock Eval7S machine (Table 4 and Table 5). The results are within the accepted change range with no significant variance beyond. Results showed negligible differences across the pyrolysis parameters. S1 values from the standards are very similar with ± 0.07 mgHC/g. On the other hand, S2 from the same IFP 160000 standard shows ± 0.01 mgHC/g difference, which is in the range of the accepted fluctuation. Furthermore, T_{MAX} values report 416°C across the different standard runs as expected. Additionally, TOC measurements are also in the accepted range with a very minor difference of $\pm 0.3\%$ (Table 4). In addition, pyrolysis results from the duplicated samples (Sample 2 and Sample 5) showed consistent results over the three cores with very minor differences (Tables 5, 10, 13, 16, 19, 23, 26, 29, 32, 36, 39, 42, and 45).

Despite these consistent results, there are several samples that were excluded from this interpretation as results show outliers due to different technical reasons including contaminants from drilling fluid, and the very low organic content in the sample. Sample 4 from Core 1 shows outliers in T_{MAX} values through the different time runs (Figure 7). T_{MAX} values received demonstrate a wide scatter (152-599°C) and are relatively low as an average compared with the other three samples from the same core

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(average T_{MAX} is 465°C). The anomaly in T_{MAX} is affected by the low TOC content (>2.0% TOC) in Sample 4. It is worth mentioning that Sample 4 was taken from a laminated, light color, high illite concentration, highly cemented concretion with calcite and low organic section from Core 1 (Figure 19). This sample shows lean to non-source rock facies and is not representative of Core 1. Samples with low organic content normally require less time during pyrolysis combustion and the rapid sample consumption produces a small S2 peak making the interpretation of T_{MAX} difficult and un-precise. Low TOC and S2 peak determination issues were reviewed by Yang et al. (2020) as the uncertainty of T_{MAX} in revealing the thermal maturity of organic rock. Yang highlighted several experimental issues related to the model of the Rock-Eval instrument That can define the quality and reliability of T_{MAX} data such as sample loading and the form of the pyrolysate (S2) peak(s).

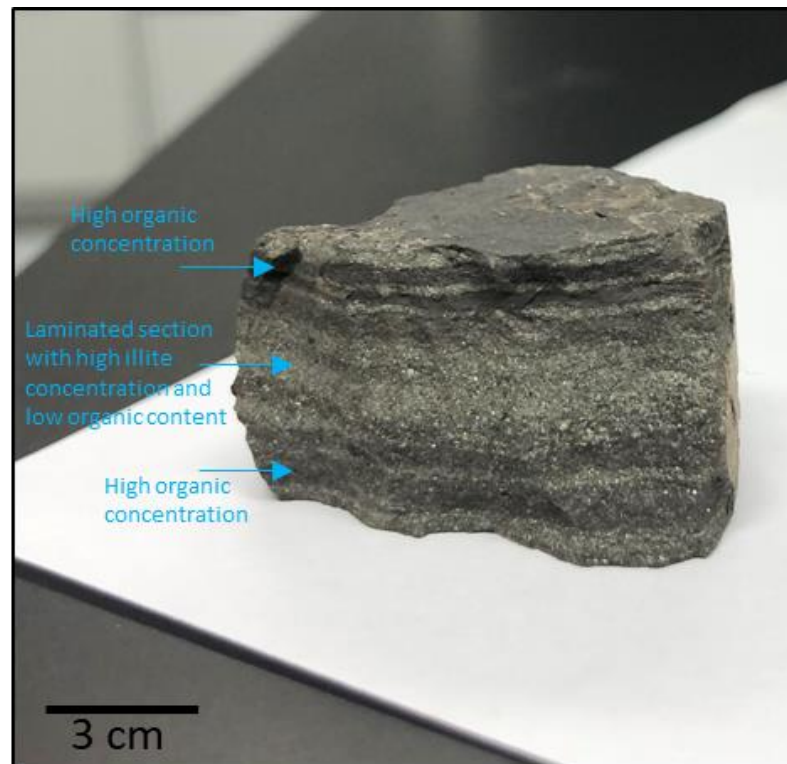


Figure 19: Sample 4 was taken from a laminated, light in color, high muscovite concentration, concretion, highly calcite cemented and low organic section from Core1.

Core 2 also shows similar outliers within T_{MAX} values in Sample 1 over the different time runs (Figure 12). Those anomalies are associated with low S_2 values from the same sample. T_{MAX} values are relatively low compared with the other three samples from the same core. Average T_{MAX} values from Sample 2, Sample 3, and Sample 4 are 467°C , while results from Sample 1 show average T_{MAX} values of 385°C (Figure 12). The values from Sample 1 were changing in a very narrow range until the three weeks-cycles run (3W). After that, values start to increase toward the other samples value (Figure 12). Results at 0h run (fresh sample) from the four samples show also outliers with low T_{MAX} values similar to Sample 1 case (Table 27). The values jump and then change in a narrow range immediately after one hour. This increase was in a plateau trend up to 4 months test (Figure 12). Those observations highlight the valid effect of

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the outer surface in the four collected samples and can be illustrated through the comparison with the outer surface samples results that were taken from the same core (Table 27).

The three cores were drilled using water-based mud with organic chemical additives. Core 2 is could be demonstrated that organic additives to drilling mud can be detected on pyrolysis measurements including T_{MAX} and S_2 values which override the rock values (Figure 12). With increased time, samples that were taken from deeper intervals during the onward time tests such as after 1 hour (1h), 2 hours (2h) and so on, have proved that the obtained samples have avoided any contaminants from drilling and the outer surface (Figure 20). This situation has clearly occurred after three weeks as samples were taken from deeper intervals from the Sample1 location (Figure 12). To support this more, the four samples at 0h time show similar T_{MAX} values (388°C) values to the sample 1 case. The four samples were most likely affected by the outer layer as samples were taken from areas close to the outer surface. Three other samples demonstrated different results, (Sample 2, Sample 3, and Sample 4) during the next runs (Figure 12). Results after one hour (1h) had back with comparable T_{MAX} readings unlike Sample 1. This challenge was highlighted along with water-based drilling impact on geochemical evaluation by Wenger et. al 2004. Wenger observed that water-based drilling fluids that are used for deep-water operations contain organic based additives that may impact fluid and rock geochemistry. The additives are often a significant component of water-based muds, they may affect or be measured in the geochemical signature of fluids and rocks.

Results from Core 3 show more comparable results in S1, S2, T_{MAX} and TOC values (Figure 15, Figure 16, Figure 17 and Figure 18). From the lesson learned from previous samples, the core was cleaned well by taking out a good portion from the outer surface using sand papers prior to sampling, and was collected from deeper locations to avoid any contaminates. Results show no outliers from the four samples across the different time runs.

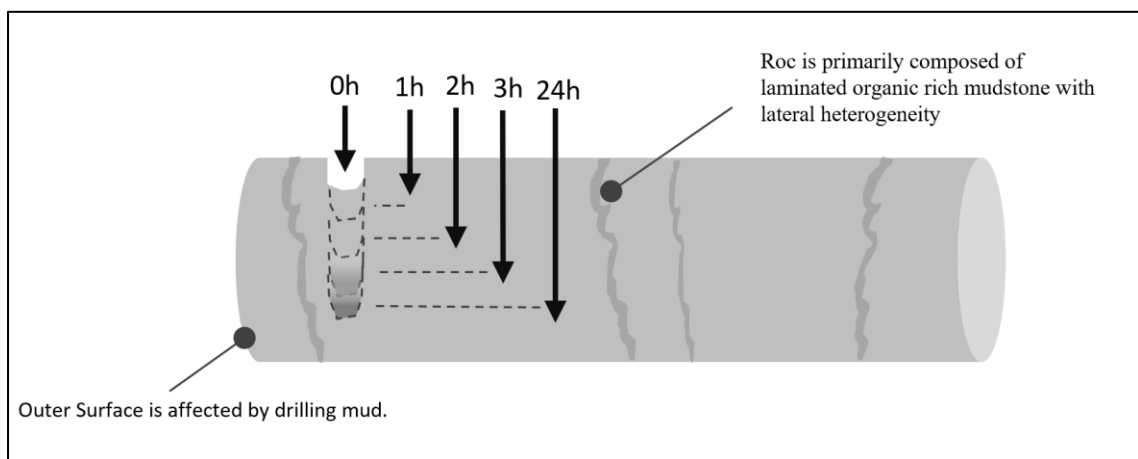


Figure 20: Schematic drawing showing the different locations of the samples taken from the preserved cores and their effect on the results over time. The anomalies detected in pyrolysis results could highlight the valid effect of the outer surface and drilling mud in the collected samples. In addition, the fluctuations in pyrolysis parameters are most likely due to lateral changes in microfacies and the distribution of organic matter across the core interval.

5.2 Long-term Preservation Impact

Overall, results from the three preserved cores (C1, C2 and C3) for up to 4-5 months-time cycles (4-5 months of storing time) show very minor changes over time. S1(Figure 5, Figure 10, and Figure 15), S2 (Figure 6, Figure 11, and Figure 16), TOC (Figure 8, Figure 13 and Figure 18) and T_{MAX} values (Figure 7, Figure 12 and Figure 17) show accepted fluctuation ranges which they could indicate the impact of the sampling

position, which also reflects the lateral heterogeneity in the laminae at the micro-scale for the three cores. Furthermore, those minor changes in the pyrolysis parameters with time could also be attributed to the storage condition due to different storing conditions (store temperature) for the three cores (Figure 4, Figure 9 and Figure 14).

5.2.1 Un-Preserved Samples Comparison

The three cores (C1, C2 & C3) were drilled or extracted in a relatively similar time in 2022 (Table 1). A portion from each of these cores (1-foot length) was selected and waxed immediately after cores have reached the surface. The remaining portions of the cores were kept unpreserved (unwaxed and uncovered) and exposed to normal surface conditions before storage (Table 46).

Table 46: Cores information: drilling and testing dates.

Core ID	Drilled Date	Test Date for Un-preserved	Test Date for Preserved	Preservation Duration
C1	Jan, 2020	March, 2020	Sept, 2022	619 Days
C2	Jan, 2020	March, 2020	Sept, 2022	634 Days
C3	Jan, 2020	Nov, 2020	Oct, 2022	661 Days

The pyrolysis results from non-preserved cores are utilized following a similar sampling protocol for a reasonable comparison with results from the preserved sections. The un-preserved samples were taken from a one-foot homogenous interval above and another one-foot below the preserved sections used in this study (Figure 2). The two feet from each core represent the non-preserved section of the core. The un-preserved samples were tested for pyrolysis using a source rock analyzer instrument (SRA) and LECO for TOC measurements (Table 47).

Table 47: Pyrolysis results from the un-preserved samples.

Core ID	TOC %	S1 mg/g	S2 mg/g	S3 mg/g	TMAX °C	HI	OI	PI
C1 - UP01	4.00	1.72	3.28	0.22	476.06	82.05	5.50	0.34
C1 - UP02	1.30	0.36	0.39	0.22	450.00	30.00	16.92	0.48
C2 - UP01	2.07	1.10	1.32	0.34	475.44	63.83	16.44	0.45
C2 - UP02	1.63	0.90	1.07	0.17	474.58	65.77	10.45	0.46
C3 - UP01	3.43	2.95	3.72	0.21	470.50	108.31	6.11	0.44
C3 - UP02	4.53	2.38	4.01	0.25	467.70	88.59	5.52	0.37

The preserved samples were tested using Rock-Eval 7, while the un-preserved samples were tested in different laboratories with different instruments (SRA for pyrolysis and LECO for TOC). Using different lab instruments in the two data set was considered during the data comparison. Data sets from the two labs were comparable and within the expected range in terms of thermal maturity and organic richness. Previous studies showed narrower, and smaller values for standard deviation between different organic geochemical laboratories and methods. (Birdwell et al., 2019). The study by Behar et al. 2015 showed a comparison with TOC determined by the Leco instrument and Rock-Eval 6 with a very good correlation for more than 89 samples with a correlation coefficient of 0.998. Although the two methods, LECO TOC and Rock-Eval TOC differ substantially in sample preparation and measurement itself, they are expected to provide comparable results to each other (Behar et al. 2001).

A comparison between results from preserved and unpreserved samples was completed to evaluate the preservation quality and to determine any significant changes with time. Results from unpreserved samples from Core 1 show significant changes compared with the average preserved samples from the same core (Figure 21). The quantity of organic content that are represented by TOC, S1 and S2 are slightly varied between the

un-preserved two feet in Core1 (C1-UP01 & C1-UP02). UP01 sample is relatively higher in TOC with 4%, while UP02 is 1.30% (Table 47). Furthermore, S1 and S2 are 1.72 mgHC/g and 3.28 mgHC/g respectively in UP01, while UP02 shows S1 and S2 values of 0.3 mgHC/g and 0.39 mgHC/g respectively (Table 47). This TOC variation gives similar wide distribution to the TOC range as of the four preserved samples that were tested from Core 1 (1.5-12.0% TOC) (Table 7). Sample 1 and Sample 2 are slightly higher in organic content compared to Sample 3. Therefore, for Core 1 and to achieve a more realistic comparison. UP01 (un-preserved sample) is more comparable to both Sample 1 and Sample 2 (preserved samples), while UP02 (un-preserved sample) is more toward Sample 3 (preserved sample).

Overall, Core 1 shows a drop in S1 values comparing preserved and non-preserved samples. Resulted values from high organic samples drop from 4.2 mgHC/g which is the average S1 for Sample 1 and Sample 2 (Table 7) to 1.72 mgHC/g which is the S1 value from sample UP01 (Table 47). Results from the low organic sample drop from 2.8 mgHC/g which is the average S1 for sample 3 (Table 7) to 0.36 mgHC/g which is the S1 value from sample UP02 (Table 47). The reported drop in S1 values is relatively lower in high organic samples (Sample 1 and Sample 2) compared with the low organic sample (Sample 3). S1 decreased by almost 59% in high TOC samples and by 87% in low TOC samples (Figure 21).

Core1 also shows an associated drop in S2 values between preserved and non-preserved samples. Values from high organic samples drop from 7.9 mgHC/g which is the average S2 for Sample1 and Sample 2 (Table 7) to 3.28 mgHC/g which is the S2 value from sample UP01(Table 47). The values from the low organic sample drop from 3.1

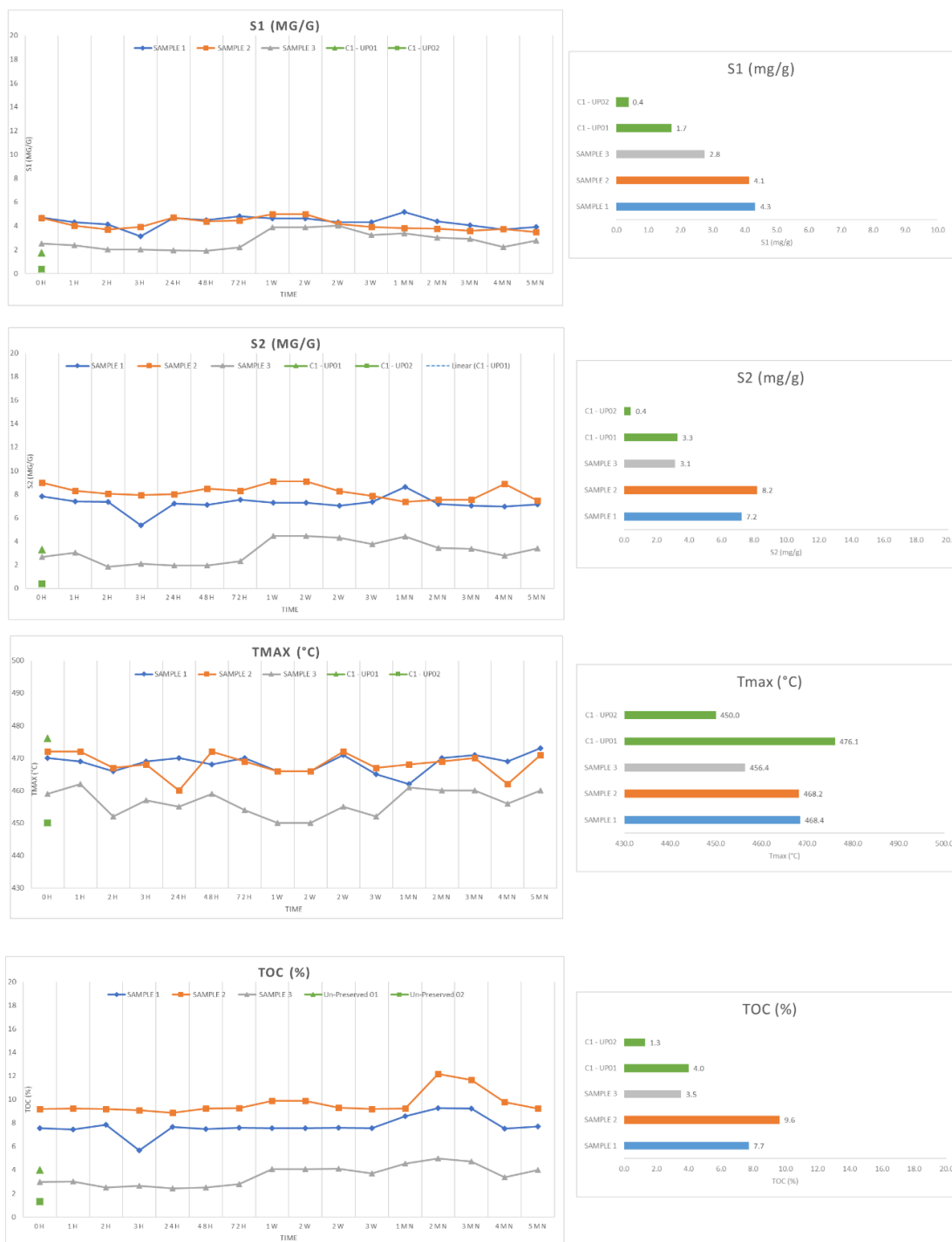
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mgHC/g which is the average S2 for Sample 3 (Table 7) to 0.39 mgHC/g which is the S2 value from sample UP02 (Table 47). This drop follows a similar trend compared with the S1 drop from the same core. And similarly, the changes of S2 values in high organic samples was relatively lower ($\Delta 58\%$) compared with the drop in low organic sample ($\Delta 87\%$) (Figure 21).

The T_{MAX} was also affected by preservation due to changes in S1 and S2 values. Average value from high organic samples is 468°C , which is the average T_{MAX} for Sample1 and Sample 2 (Table 7), while the value from sample UP01 is 476°C (Table 47). in the other hand, values from low organic sample shows 456°C , which is the average T_{MAX} for Sample 3 (Table 7), and value from sample UP02 is 450°C (Table 47).

TOC values show changes between preserved and non-preserved samples. Values from high organic samples drop from 8.7% which is the average TOC for Sample1 and Sample 2 (Table 7) to 4.0 %, which is the TOC value from sample UP01 (Table 47). Values sample with low organic content drops from 3.5% which is the average TOC for Sample 3 (Table 7) to 1.3%, which is the TOC value from sample UP02 (Table 47). similarly, the changes in high organic sample was relatively lower (54%) compared with the drop in low organic sample (62%) (Figure 21).

Figure 21: Comparisons between results obtained from preserved and un-preserved for Core 1. Results from unpreserved samples from Core 1 show significant changes in S1, S2 and TOC values compared with the average preserved samples from the same core. In addition, T_{MAX} values were also affected by preservation due to changes in S1 and S2 values. C1-UP01 & C1-UP02 are two unpreserved samples from Core 1, while Sample 1, Sample 2 and Sample 3 are preserved sample from Core 1.



Core 2 results show also similar significant changes compared with the preserved samples from the same core (Figure 22). Unlike Core 1, this core shows a narrower range of organic content values (min TOC is 2.7%, max TOC is 3.8%) (Table 20); and similarly, un-preserved samples show also a narrower range in terms of organic content that are represented by TOC, S1 and S2 peaks (Table 47). UP01 shows 2.07% TOC and UP02 is 1.63%. Furthermore, S1 and S2 are 1.10 mgHC/g and 1.32 mgHC/g respectively in UP01, while UP02 shows S1 and S2 values of 0.90 mgHC/g and 1.07 mgHC/g respectively. This narrow range shows a similar distribution range to the four preserved samples that were tested from Core 2. Average TOC in the four preserved samples is 3%. S1 & S2 are 2.3 mgHC/g and 3.1 mgHC/g respectively; and the T_{MAX} average is 467°C (Table 20).

Overall, Core 2 shows a similar drop in S1 values between preserved and non-preserved samples as observed in Figure 20. Values from preserved samples drop from 2.3 mgHC/g, which is the average S1 for Sample1, Sample2 and Sample3 (Table 20) to 1.0 mgHC/g, which is the average S1 value from samples UP01 & UP02 (Table 47). The results also show a drop in S2 values between preserved and non-preserved samples. Values from the preserved core drop from 3.1 mgHC/g, which is the average S2 for Sample 1, Sample 2 and Sample 3 (Table 20) to 1.2 mgHC/g, which is the average S2 value from samples UP01 & UP02 (Table 47). The changes between preserved and unpreserved samples in S1 and S2 values are around 56% and 32%, respectively (Figure 22). Results in thermal maturity value show slight changes in T_{MAX} values between the preserved and non-preserved samples. Average T_{MAX} for Sample 1, Sample 2 and Sample 3 is 467°C (Table 20), while the average value from samples UP01 and UP02

is 475°C (Table 47). Core 2 results show also a slight drop in TOC values between preserved and non-preserved samples. Average TOC for Sample 1, Sample 2 and Sample 3 is 3.0% (Table 20). This value drops to 1.85% (average value from UP01 & UP02) in the unpreserved sample (Table 47). The change in TOC between preserved and unpreserved samples is around 38% (Figure 22).

Figure 22: Comparisons between results obtained from preserved and un-preserved for Core 2. Overall, Core 2 shows a drop in S1, S2 and TOC values between preserved and non-preserved samples. In addition, T_{MAX} values were also affected by preservation due to changes in S1 and S2 values. C1-UP01 & C1-UP02 are two unpreserved samples from Core 2, while Sample 2, Sample 3 and Sample 4 are preserved sample from Core 2.



Core 3 results show minor changes with negligible differences between preserved and un-preserved results with no major change in S1 values (Figure 23). Values from preserved samples is 2.7 mgHC/g, which is the average S1 for the four preserved samples (Table 33). While UP01 and UP02 show a value of 2.95 mgHC/g and 2.38 mgHC/g (Table 47). Results show also a similar trend with S2 values between preserved and non-preserved samples. Values from preserved samples show no major change in S2 values. Average S2 value from the preserved samples is 5.0 mgHC/g (average S2 for the four preserved samples) (Table 20). While UP01 and UP02 show average values of 3.72 mgHC/g and 4.01 mgHC/g (Table 47). In addition, results from preserved samples show a T_{MAX} average value of 457°C (average T_{MAX} for the four preserved samples) (Table 20). While UP01 and UP02 show average values of 470.5°C and 467.7°C (Table 47). Finally, Core 3 shows also a negligible change in TOC values between preserved and non-preserved samples. The average TOC for Sample1, Sample 2, Sample 3 and Sample 4 (preserved samples) is 4.3% (Table 20), whereas TOC average values from UP01 and UP02 are 3.43% and 4.53%, respectively (Table 47).

Figure 23: Comparisons between results obtained from preserved and un-preserved for core3. Core 3 results show minor changes with negligible differences between preserved and un-preserved results with no major change in S1, S2, T_{MAX} and TOC values. C1-UP01 & C1-UP02 are two unpreserved samples from Core 3, while Sample 1, Sample 2, Sample 3 and Sample 4 are preserved samples from Core 3.



These observations from the comparison results between preserved and un-preserved samples can be summarized and correlated with the thermal maturity and organic content variations (Table 48).

Overall, S1 values from the three cores (C1, C2 and C3) show significant changes in the unpreserved samples illustrated by the comparisons between preserved and non-preserved samples (Figure 21, Figure 22, and Figure 23). Through the three cores, S1 values decline with a gradual dropping trend which is ranged from 23-87% out of the total S1 reported from preserved samples (Figure 21, Figure 22, and Figure 23). This variation in S1 losses can be correlated with thermal maturity variation (Table 2). High thermal maturity cores (Core 1 and Core 2) report higher S1 drops (56%-87%) (Figure 21, and Figure 22). On the other hand, Core 3 with a relatively less thermal maturity level shows few S1 losses with only 23% out of the total reported S1 (Figure 23). Furthermore, TOC variation seems to have no clear control over the S1 losses through the three cores (Table 2). The correlation between S1 losses and TOC was not proved during this comparison (Table 48).

S2 values demonstrated a dropping trend similar to S1 with time. Through the three cores (C1, C2 and C3), S2 values report a decline illustrated by the comparisons between preserved and non-preserved samples (Figure 21, Figure 22, and Figure 23). This drop is close enough to the S1 drop with a comparable amount of losses. Greater losses in mass are reported in high thermal mature cores (C1 and C2) with 32-87% out of the total S2 values (Figure 21, and Figure 22). While the relatively low thermal maturity core (C3) reports a lower S2 drop with 23% out of the total S2 values (Figure

23). And similar to S1, this comparison couldn't prove the correlation between the S2 losses and organic richness (TOC) (Table 48).

T_{MAX} values show an increasing trend with time through the three cores (Figure 21, Figure 22, and Figure 23). This change is reported in a very narrow range between 6-8°C degrees over 2 years with no sample preservation protocols. With this narrow change, a comparison is not adequate to prove any correlation with either thermal maturity or organic richness (TOC) (Table 48). T_{MAX} is affected by the change in S1 and S2 mass, as smaller quantities require less time to pyrolyze during the continuous temperature ramp. Thus, the T_{MAX} peak will inaccurately be picked through the lab instrument as the S2 peak is relatively lower in values with wider and broad shapes (due to time dependency and p temperature ramp cycle).

TOC values show a significant change with time. This is illustrated by the comparisons between preserved and non-preserved samples (Figure 21, Figure 22, and Figure 23). In high thermal maturity cores (C1 and C2) TOC results report a decline with a 38-62% drop out of the total TOC reported in preserved samples (Figure 21, and Figure 22). While the low-maturity cores report only 7% losses out of the total TOC (Figure 23). Moreover, similar to other pyrolysis parameters, TOC has no clear control over the reported losses as there is no correlation with TOC variations. This TOC drop is reasonable due to the losses in S1 and S2 values that heavily contribute to the total organic content (Table 48).

Table 48: Summary of pyrolysis changes related to the variations in thermal maturity and organic richness in the three study cores.

Core ID	Relative Organic Richness	Relative Thermal Maturity	$\Delta S1\%$	$\Delta S2\%$	$\Delta T_{MAX}^{\circ C}$	$\Delta TOC\%$
C1	High (8.0% TOC)	High (465-470°C)	59	58	8	54
	Med (3.5% TOC)	High (465-470°C)	87	87	6	62
C2	Med (3.0% TOC)	High (465-470°C)	56	32	8	38
C3	Med (4.5% TOC)	Low (455-450°C)	23	23	8	7

Similarly, these observations were noticed and reported by Zeng (2021). By using 5 fresh shale cores with five crude oil from the same well. Zeng stated that the total weight losses increase with the increase in shale maturity and oil API gravity. The total weight losses of S1 were reported up to 70%. Additionally, Noble et al. (1997) and Micheal (2014) reported that Hydrocarbon weight loss is a function of the oil API gravity. The lighter the oil in the rock, the greater the component of C15 minus the fraction that is lost. The correlation with density (API gravity) is only approximate as density is controlled at the molecular level (Michael, 2014).

A similar study was performed by Bhosle (2015) to determine the effect on sample holding time although, the condition of those samples was not stated or defined. Bhosle noted that samples were processed at three days, four weeks and after 12 weeks. Among the 15 samples, only two samples can be taken as solid with more reliable measurements due to the low organic content measured from these samples. Low organic measurements can negatively affect the other pyrolysis measurements. Results show that there is a very slight to negligible change in S1 and S2 values with less than

1.0 mgHC/g after 12 weeks. In addition, a negligible with a slight jump in T_{MAX} was reported with 2°C after 12 weeks.

Jiang (2015) observed a significant evaporative loss during core handling and storage as well as sample preparation before analysis. The study stated that there is a significant evaporative loss of light hydrocarbons which can take place within hours or during crushing samples. Results show that samples after 21 hours and after one week of handling exhibit a very slight change. A slight drop in S1 value after 21 hours and after one week ranged from 0.17-0.10 mgHC/g, and similarly the drop in S2 values ranged from 0.04-0.09 mgHC/g. Additionally, T_{MAX} increased with 0-2°C with negligible fluctuation in TOC with a difference ranging from 0.03-0.16%.

5.2.2 Storing Temperature Impact

In order to highlight the storing impact on core samples with time, the storing conditions and the temperature for the three cores during this study were used.

The three cores were drilled in the same year (Jan, 2020) and kept preserved for between 619-661 days in a shaded core store (Table 1). After 2 years of cores preservation, the three cores were opened with almost comparable weather temperatures. Core 1 and Core 2 were opened in September 2022 with an outside weather temperature that is ranged between 40-45°C (Figure 4 and Figure 9). The cores were left open (unpreserved) for 182-183 days for time-cycles lab runs. Similarly, Core 3 was opened in

a relatively lower outside weather temperature with an average of 37°C. This core is kept open (un-preserved) for 151 days (Figure 14).

The ambient temperature between preservation time for the three cores was vary and ranged between 37-45°C. The ambient temperature was recorded for the three cores during this study in a daily base before sampling (Figure 4, Figure 9 and Figure 14). This variation could explain the small but measurable variations reported in the results from the three cores. Results from the three cores followed a similar fluctuation trend with the time that was illustrated through the different pyrolysis parameters (S1, S2, TOC and T_{MAX}) (Figure 5, Figure 6, Figure 7, Figure 8, Figure 10, Figure 11, Figure 12, Figure 13, Figure 15, Figure 16, Figure 17, and Figure 18). Overall, the preserved samples from the three cores haven't displayed significant changes in pyrolysis parameters with time. The cores after opening the wax seal were stored in a shaded core store to protect the samples from air humidity, or any direct heat (sunlight). Core1 was exposed to weather temperature that averaged 23°C (store temperature) (Figure 4), Core 2 was exposed for a weather temperature that is averaged of 22°C (store temperature) (Figure 9), while Core 3 was exposed to a weather temperature that is ranged from 37-10°C with an average of 19°C (store temperature) (Figure 14). Overall, the three cores were stored in normal to low temperature environments with no heat or humidity exposures.

5.2.3 Preservation Quality

The hydrocarbon loss has been reported not just from un-preserved cores, but also in very minor amounts from the preserved cores. At well site, cores are layout for few minutes before they are completely preserved with foil, plastic and wax layers. During this time, changes are expected in cores and its fluids (Steiner, 2016). Generally, most of the organic solvent evaporated from samples within first day with a negligible change in weight thereafter (Gupta, 2017). Additionally, the fluid content from reservoir to surface is subject to alteration that cannot be avoided with wax preservation method. In case of water-based mud operation (which was used in the core collection used in this study), the water saturation is expected to gradually being more pronounced after coring operation as a result of flushing the core with drilling mud. The change in the water saturation from water-based muds is estimated (Bajsarowicz, 1992) to be up to 40%. Furthermore, this change is followed by another hydrocarbon fluids alteration that is functioned by a shrinkage factor and a formation volume calculation during the trip to surface. The hydrocarbon saturation drops from subsurface to surface condition is estimated with 20-22% (Bajsarowicz, 1992).

Despite these uncontrolled factors, some researchers had also recommended other preservation methodologies rather than the wax method to reduce the in-situ fluid losses. For example, test results from the North Sea example by Skopec, 1995 using a downhole gel core preservation method showed no base oil invasion had occurred in center plugs, even in sections with permeabilities > 1 Darcy. During this method, a high molecular weight polypropylene glycol is used. Laboratory tests indicate no loss and

zero water loss at 200F and 250 psig on water-saturated gel-coated rocks with permeabilities as great as 10 Darcys (Skopec,1995).

5.3 Implications on Source Rock Assessment

Core samples are commonly used as the source of information for characterizing a reservoir, basin modelling, and general geological studies. Serious issues during core preservation and storage can cast uncertainty on the results of such studies. Source rock evaluation and resource assessment through pyrolysis analysis is significantly affected by the free hydrocarbon (S1) losses due to poor core preservation and release of gasses at the surface. The hydrocarbon losses will result in less reliable measurements and non-representative properties of the actual reservoir rocks, particularly acute in the S1 value.

The diagnostic parameter for moveable hydrocarbon content in shale oil is the oil saturation index (OSI) that Jarvie (2012) has proposed. This approach is a function of the free hydrocarbon in the rock that is presented by S1 through rock eval pyrolysis. There is a large error between the measured S1 and the actual underground in-situ value, which becomes more pronounced the higher the gas content increases (Xianzheng, 2021). The non-representative S1 values due to losses and inadequate preservation can be misleading in dealing with such pyrolysis proxies to identify any subsurface potential.

In unconventional rocks, the free hydrocarbon portion is used to determine the volume of oil that is present. The S1 parameter, resulting from Rock-Eval pyrolysis

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measurement, reflects “free” hydrocarbons contained in a rock sample. The specifics of shale formations saturated with liquid hydrocarbons make it possible to undertake the task of oil-in-place assessment. This can be achieved by taking advantage of direct geochemical measurements of hydrocarbons contained in rock samples collected from liquid-rich shale intervals. However, the most important issue of each resource or reserve assessment method is its credibility. The lightest compounds and light liquid hydrocarbons evaporate completely or partially in surface conditions due to the core sample handling procedure.

Adding to this, there is a significant issue in calculating the in-place resource as traditional resource estimates may not consider a full correction for evaporative loss, particularly for the gaseous oil lost during coring (Li et al. 2020). The estimation of oil-in-place reserves considering evaporation loss can be expressed by the introduction of the correction coefficient. Those oil-in-place estimations on the basis of S1 values directly are facilitated by the introduction of appropriate correction coefficients for hydrocarbon losses, which is dependent on oil API gravity and shale rock maturity level. Sowizdzal (2020) showed that calculation equations for oil-in-place based on rock eval pyrolysis must account for substantial underestimations, as the S1 parameter reflects only a part of hydrocarbon compounds originally present in shale rock at reservoir conditions. Thus, correction coefficients were determined with laboratory analytical procedures, enabling adjustment. Furthermore, Abrams et al. (2017) added a term (S1Loss) for the evaporative loss in the total oil yield equation to emphasize the importance of correcting the loss in resource evaluation. The S1 loss can be estimated by knowing the density of the hydrocarbon fluid in-place, which can be estimated from

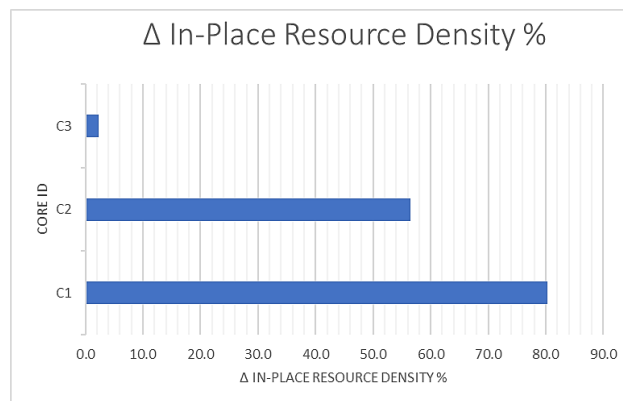
the whole oil extract gas chromatogram or estimated from relationships based on biomarker compounds (Michael et al. 2013). Adding to this, a calculation method for the evaporative hydrocarbon recovery coefficient based on the formation volume factor has been proposed by Guo (2020). The original quantity of underground shale oil can be calculated by knowing the viscosity of subsurface oil through the PVT sample and the density of the subsurface oil. While the quantity of the surface shale oil can be calculated by multiplying the surface oil density with the surface oil viscosity at 50C the dimensionless evaporative hydrocarbon recovery coefficient can be estimated (Equation 1). Where k_{S1} is the dimensionless evaporative hydrocarbon recovery coefficient, Q_{or} is the original quantity of underground shale oil in tonnes, Q_{pd} is the quantity of surface shale oil in tonnes, V_{sub} is the volume of underground shale oil in a cubic meter, V_{pd} is the volume of surface shale oil in a cubic meter, B_o is the dimensionless crude oil volume factor, P_{sub} is the density of formation oil in tonnes per cubic meter, and P_{pd} is the density of surface oil in tonnes per cubic meter.

$$k_{S1} = \frac{Q_{or} - Q_{pd}}{Q_{pd}} = \frac{V_{sub}}{V_{pd}} \times \frac{\rho_{sub}}{\rho_{pd}} - 1 = B_o \times \frac{\rho_{sub}}{\rho_{pd}} - 1 \quad (1)$$

Re-calculating the in-place resources using the corrected S1 values from preserved samples testes with S1 values that ranged from 2.3-4.3 mgHC/g show a significant difference compared with the in-place resources calculated using S1 values from unpreserved samples (average S1 is 1.8 mgHC/g). (Figure 24). This test attempts to emphasize the importance of using representative samples with the least uncertain values to achieve reasonable and representative value.

Using Downey's 2011 equation in calculating oil in place (OIP) for tight reservoirs using simple Rock-Eval S1 values. A comparison of in-situ hydrocarbon volumes from preserved samples and non-preserved samples from core1 show a difference of 80% in resource density. The resource density drops as a result of losing S1 mass with time. Furthermore, comparison results from core2 using the same equation calculated using S1 from preserved samples and un-preserved samples show a similar trend with a 56.5% difference. Finally, results from Core 3, which had illustrated negligible changes in S1 values between preserved and non-reserved results in this study show only a 2.3% difference in the calculated resource density using the same equation. Those differences came close enough to the same attempts that were done by Michael (2014) in calculating the resource density using corrected and uncorrected S1 values. The calculated resource density had shown a significant drop when using the uncorrected S1. The difference had reached to 66% (200bbls/acft) between using corrected and uncorrected S1 value. Furthermore, the study by Michael (2014) had touched the sensitivity of S1 correction to API gravity. Results had also shown that the difference in in-place resources in high mature fluids (40 API with 125bbls/acft) is higher by 15% compared with relatively lower mature fluid (35API with 100 bbls/acft).

Figure 24: Re-calculating the in-place resources using the corrected S1 values from preserved sample tests.



Chapter 6

Conclusion

6.1 Summary & Conclusion

Good preservation of cores plays a key role in protecting rock materials and their fluid contents, minimizing any physical and chemical alterations of rock samples during long storage periods. Results proved that pyrolysis parameters are affected by the preservation process and its duration. Pyrolysis results from core samples that were preserved over two years after drilling show insignificant changes over time up to 4-5 months with no preservation. S₁, S₂, TOC and T_{MAX} show very minor changes that are interpreted as a result of the lateral heterogeneity in the 1-foot core (Figure 5, Figure 6, Figure 7, Figure 8, Figure 10, Figure 11, Figure 12, Figure 13, Figure 15, Figure 16, Figure 17, and Figure 18). On the other hand, pyrolysis results from un-preserved samples that were measured after 90 days for Core 1 and Core 2 and 300 days for Core 3 (Table 46) show a significant drop over time. Comparison between pyrolysis results obtained from those un-preserved samples and the preserved samples show a decrease in S₁, S₂ and TOC values over time for the un-preserved samples. In addition, T_{MAX} was also affected by the change in S₁ and S₂ values with a slight increase in T_{MAX} values (Figure 21, Figure 22, and Figure 23). The findings of this study can be summarized as follows:

- Insignificant changes were observed in the pyrolysis results obtained from preserved core samples. However, coating core samples with hot wax or strippable plastic is better completed as soon as brought to the surface (after coring), and changes in the core's content are expected during those wellsite processes. Therefore, performing an appropriate analysis immediately after conventional coring can maintain the detection of light oil components accurately in shale cores.
- Pyrolysis results from the unpreserved samples that were left exposed to normal conditions for 90-300 days after drilling showed significant changes in pyrolysis compared to preserved samples from the same interval. Comparison results show that S1 and S2 drops by up to 87% over the observation time interval, while TOC measurements showed a drop that reached 62%.
- The slight increase in T_{MAX} values over time is possibly controlled by the changes in S1 and S2 mass, as smaller quantities require less time to pyrolyze during the continuous temperature ramp. Thus, the T_{MAX} peak will inaccurately be picked through the lab instrument as the S2 peak is relatively lower in values with a wider and broad shape (due to time dependency and programmed temperature ramp cycle).
- Hydrocarbon loss is a function of thermal maturity and the coring and sampling procedure. The lighter the hydrocarbon in the rock the greater the lost amount. This was illustrated by the amount of losses reported from Core 3 as most of the losses possibly occurred during core handling at the wellsite.

- The variation in an ambient temperature between preservation times can explain the measurable variations reported in the results from the three cores. Core 3, which was preserved at cooler ambient temperatures and exhibited less S1 & S2 losses compared with the other two cores.
- Results from this study showed that the variations in hydrocarbon losses have been reported not just from the un-preserved cores, but also from the preserved cores. However, results from preserved samples show very minor differences with negligible changes.
- The hydrocarbon losses will result in less reliable measurements and non-representative properties of the actual reservoir rocks, particularly acute in the S1 value. Sample preservation can initiate a massive challenge while estimating oil and gas in-place volumes.
- Identifying the impact of long-term rock sample storage and preservation on source rock geochemical results can help to constrain a data correction model, reduce uncertainty, and suggest an ideal workflow for better future coring and preservation plans.

6.2 Future Studies

The evaporative hydrocarbon loss from cores even with proper core preservation methods suggests further research should be undertaken to minimize their implications on the wide geochemical applications. Determination of the exact quantity of substance lost from rock samples at the surface is a critical issue for ensuring accurate in-situ

conditions. Various efforts in the past have been devoted to addressing the problem of so-called S1 “carry-over” due to either large molecular heavy oil and bitumen residue or migrated oils in samples, causing S1 responses from pre-existing hydrocarbons occurring in the default temperature range of the S2 curve (e.g., Jarvie, 2012; Sanei et al., 2015; King, 2015; Li et al., 2018; Chen et al., 2018; Romero-Sarmiento et al., 2016, 2017; Romero-Sarmiento et al. 2016,2017; Li, et al. 2020). Identifying the original hydrocarbon components in the rock sample that are representatives of S1 and S2 peaks is critical to detect the lost components with time.

Jiang (2015) has illustrated the absence of $<nC_{12}$ hydrocarbon components from shale samples due to the evaporative loss to its light-end hydrocarbons during core handling and storage as well as sample preparation before analysis. Both the Rock-Eval S1 peak values and molecular compositions were compared among a freshly prepared core sample. The freshly ground shale sample contained abundant hydrocarbons as light as C_3 to C_4 . However, most of the C_3 - C_7 hydrocarbons were absent just after a week of storage in a capped vial. In addition, his (who?) study showed a partial loss of higher molecular weight hydrocarbons such as C_{11+} . Furthermore, Jiang et al. (2016a) showed that the oils lost during sample preparation and storage are mostly low-boiling-point hydrocarbons less than C_{12} in the diesel and gasoline-range compounds. Adding to this, Michael (2014) stated that hydrocarbon loss was referred to as C_{15} minus fraction.

During pyrolysis, the thermal hydrocarbon evaporative can be detected by dividing the FID pyrogram into different parts by customizing the temperature ramp. This method can be used to identify the evaporative portion in rock samples. Li et al. (2018) divided the raw FID pyrogram into three parts. S1a detected the thermal evaporative of volatile

and black oil in a free state; S1b for the thermal evaporative with high molecular weight such as heavy oil and bitumen in sorption; and S2 for the kerogen thermal decomposition products. The light portion in addition to the sorbed portion of kerogen in the rock sample can be addressed by running the rock samples in pyrolysis before and after solvent extraction. Post-solvent extraction results demonstrated a significant decrease in the S1 peak after extraction compared to un-extracted samples (Al Eid, 2020). These changes were all attributed to the removal of S1-free hydrocarbons from the rock matrix.

Adding to this, S1 losses can be also estimated by comparing the oil masses in reservoir and subsurface conditions. Chen et al. (2019b) proposed a novel method to estimate the gas loss in S1 based on the phase behavior equation of the petroleum fluid. By comparing the oil masses in reservoir and surface conditions, the difference represented the quantity of gas missed in S1.

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