

Experimental Study of the Impact of Extended Storage Times, Delayed Sample Processing, and Poor Preservation on Source Rock Geochemical Assessments

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Extended abstract

Abstract

Fluid loss resulting from poor preservation (evaporation and expulsion) is a significant problem in sampling source and reservoir rocks as it has a substantial impact on laboratory results. The preservation process and its duration affect pyrolysis parameters due to the mass loss of hydrocarbons over extended storage times and poor preservation. This research project aims to determine the impact of extensive sample storage times and delayed sample processing and analysis on the results obtained from geochemical analyses. To achieve optimal results and enhance uncertainty estimates when dealing with geochemical data from samples exposed to variable storage times, a specific experimental design and sample selection strategy have been implemented. Well-preserved core samples were utilized for this study, with each preserved core being individually subjected to pyrolysis using consistent time cycles. Existing pyrolysis measurements from non-preserved core samples from the same wells and the same stratigraphic intervals as the preserved cores were compared with the results obtained from the preserved samples. Overall, results from preserved samples showed no significant changes in pyrolysis parameters. However, when comparing the pyrolysis results from preserved and un-preserved core samples from the same interval, there were significant drops in free hydrocarbon (S1), potential hydrocarbon (S2), and total organic content (TOC) measurements for the un-preserved samples. These changes are attributed to hydrocarbon losses resulting from poor sample preservation prior to lab analysis. It is crucial to note that relying on unrepresentative pyrolysis measurements from samples that have been stored for a long time or poorly preserved can critically impact results used for many geochemical applications and source rock assessment.

Introduction

Source rock geochemical assessments are important for predicting the quantitative and qualitative aspects of petroleum systems. Rock geochemistry plays a crucial role in enhancing exploration efficiency by considering various factors that influence the volumes of crude oil and natural gas, such as source-rock distribution, organic richness, and thermal maturity (Al Eid et al. 2020; Karg et al. 2022; Abu-Mahfouz et al. 2019, 2022, 2023; Peters, 2022; Grohmann et al. 2023).

Accurate geochemical analysis of these rocks is critical to determine their hydrocarbon-generating potential and commercial viability. However, improper handling, poor preservation, and lengthy storage of rock cores can negatively impact the quality of source rock geochemical data. Therefore, ensuring the integrity of cores becomes paramount in accurately reconstructing the original rock conditions. Effective preservation techniques must be employed to maintain optimal sample quality during long storage periods prior to laboratory analysis. In the oil and gas industry, various core preservation methods have been utilized, including quick freezing, wrapping cores with

plastic wrap and aluminum foil followed by wax coating, sealing the core in plastic sacks, or storing core samples in plastic or metal tubes (Basan et al. 1988; Hunt & Cobb, 1988; Basu et al. 2020; Li et al. 2022).

These techniques aim to prevent breakage during handling and storage and preserve core fluids for accurate analyses. It is important to recognize that sample preservation techniques and storage times significantly influence lab analysis results (Bhosle et al. 2015). One of the major challenges in sampling source and reservoir rocks for laboratory analyses is fluid loss resulting from poor preservation, which includes evaporation and migration (Ubani, 2013). Several studies have discussed this issue and identified potential reasons for the loss of light hydrocarbons (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; Bhosle et al. 2015).

The objective of this research project is to experimentally investigate the potential impact of preservation, extensive storage time, and delayed sample processing and analysis on the results obtained from geochemical analyses. Specifically, the study aims to identify any significant differences in the results of basic source-rock geochemical screening analyses after different storage times, while highlighting the main factors that influence the analytical results. Additionally, the study aims to examine how both proper and poor preservation practices can affect these results.

By analyzing the influence of different storage conditions and preservation methods on the results of basic geochemical screening analyses, valuable insights can be gained regarding the reliability and accuracy of geochemical data. The findings of this study will contribute to improving the quality control procedures for rock core preservation in the oil and gas industry, ultimately enhancing the efficiency of exploration and resource evaluation.

Methodology

Source rock core samples were extracted from two different wells drilled and used in this study. Two feet of core (Core 1 and Core 2) were extracted from the same well, and one foot (Core 3) was taken from a different well. Immediately after coring, the core samples were sealed and preserved following a common practice for core preservation in the petroleum industry (Figure 1). Available initial organic matter richness data and thermal maturity variations were considered during the selection process.

More than 200 samples were acquired from the three different preserved cores selected for this study. From each core, the samples were taken from locations identified prior to the tests to ensure a consistent sampling protocol. A time schedule was set for each core to meet the planned experimental time cycles.

The analyses planned for the different time cycles included immediate pyrolysis analysis for the fresh samples at 0 hours (0h), followed by analysis after 1 hour (1h), 2 hours (2h), 3 hours (3h), 24 hours (24h), 48 hours (48h), 72hours (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) using a Vinci Rock-Eval 7S machine. Results obtained from each run were plotted to determine the effects of sample storage time and analytical delays (after sample extraction from the well) on geochemical analyses of preserved core samples.

To examine the effect of poor preservation (non-preservation) on the geochemical results of the study core samples, existing pyrolysis measurements from another set of unpreserved core samples from the same cored wells (same interval) were interpreted and compared to those obtained from the preserved cores during this study (Figure 2).

Pyrolysis Results from Preserved Cores

Each preserved core was run individually for pyrolysis through consistent time cycles. Results from each run are shown and plotted to determine the effects of sample storage time and analytical delays after sample extraction from the well. Core 1 was tested for up to 5 months following the planned time-cycle runs and was exposed (unpreserved) for 155 days since it was opened. while Core 2 had 55 samples in total tested over a 4-month time frame and was exposed (unpreserved) for 121 days from opening. Finally, Core 3 was tested over 4 months and was exposed (unpreserved) for 121 days under normal conditions. Overall, results from the three preserved cores (C1, C2, and C3) for up to 4-5 months cycles (4-5 months of storing time) show very minor changes over time. S1, S2, TOC, and TMAX values show accepted fluctuation ranges which 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, 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.

On the other hand, 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.

Preserved Vs. Un-preserved Cores

The comparison between preserved and unpreserved samples is a critical step in evaluating the preservation quality and identifying any significant changes over time in source rock geochemical assessments. The results of this study reveal significant variations between preserved and unpreserved samples collected from the same interval from Core 1 (Figure 3). While organic content, as indicated by TOC, S1, and S2, is slightly different between the unpreserved samples of Core 1 (C1-UP01 & C1-UP02), UP01 has a higher TOC content of 12 wt%, whereas UP02 has 3.9 wt%. Furthermore, S1 and S2 are 5.16 mgHC/g and 9.84 mgHC/g respectively in UP01, while UP02 shows S1 and S2 values of 0.9 mgHC/g and 1.17 mgHC/g respectively. The TOC variation in these samples is similar to the TOC range of the four preserved samples that were tested from Core 1 (4.5-12.0 wt% TOC). Sample 1 and Sample 2 have slightly higher organic content compared to Sample 3. In order to make a more realistic comparison, UP01 (un-preserved sample) can be considered comparable to both Sample 1 and Sample 2 (preserved samples), while UP02 (un-preserved sample) is closer to Sample 3 (preserved sample).

Overall, Core 1 shows a significant drop in S1 values comparing preserved and non-preserved samples. Resulted values from high organic samples drop from 12.6 mgHC/g which is the average S1 for Sample 1 and Sample 2 to 5.16 mgHC/g which is the S1 value from sample UP01. Results from the low organic sample drop from 8.4 mgHC/g which is the average S1 for Sample 3 to 1.08 mgHC/g which is the S1 value from sample UP02. 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 $\Delta 59\%$ in high TOC samples and by $\Delta 87\%$ in low TOC samples (Figure 3).

Core1 also shows an associated drop in S2 values between preserved and non-preserved samples. Values from high organic samples drop from 23.7 mgHC/g which is the average S2 for Sample 1 and Sample 2 to 9.84 mgHC/g which is the S2 value from sample UP01. The values from the low organic sample drop from 9.3 mgHC/g which is the average S2 for Sample 3 to 1.17 mgHC/g which is the S2 value from sample UP02. This drop follows a similar trend compared with the S1 drop from the same core. And similarly, the changes in S2 values in high organic samples was relatively lower ($\Delta 58\%$) compared with the drop in low organic sample ($\Delta 87\%$) (Figure 3).

The preservation of samples had a noticeable impact on the TMAX values, which were influenced by changes in S1 and S2 values. For high organic samples, the average TMAX was 473 °C, represented by Sample 1 and Sample 2. In contrast, Sample UP01 showed a TMAX value of 481 °C. On the other hand, low organic content samples exhibited an average TMAX of 461 °C, with Sample 3 representing this value, and Sample UP02 showing a TMAX value of 455°C.

The TOC values also experienced changes between preserved and non-preserved samples. The TOC values for high organic samples dropped from an average of 26.1 wt% (Sample 1 and Sample 2) to 12 wt% in Sample UP01. Similarly, the TOC values for low organic content samples dropped from an average of 10.5 wt% (Sample 3) to 3.9 wt% in Sample UP02. Notably, the drop in TOC values was relatively higher for low organic content samples ($\Delta 62\%$) compared to high organic samples ($\Delta 54\%$) (Figure 3).

Core 2 results displayed similar significant changes in preserved and non-preserved samples, as seen in Figure 4. Unlike Core 1, Core 2 exhibited a narrower range of organic content values (min TOC is 8.1 wt%, max TOC is 11.4 wt%); similarly, un-preserved samples show also a narrower range in terms of organic content that is represented by TOC, S1 and S2 peaks. Sample UP01 showed a TOC value of 6.21 wt%, while Sample UP02 had a TOC value of 4.89 wt%. Additionally, the S1 and S2 values for UP01 were 3.30 mgHC/g and 3.96 mgHC/g, respectively, while UP02 exhibited S1 and S2 values of 2.7 mgHC/g and 3.21 mgHC/g, respectively. These narrower ranges closely resembled the distribution seen in the four preserved samples from Core 2. The average TOC in the preserved samples was 9 wt%, with S1 and S2 values of 6.9 mgHC/g and 9.3 mgHC/g, respectively, and an average TMAX of 472°C. Furthermore, Core 2 demonstrated a notable, drop in S1 and S2 values that is similar for preserved and non-preserved samples. The preserved samples had an average S1 value of 6.9 mgHC/g (Sample 1, Sample 2, and Sample 3, which dropped to 3.0 mgHC/g in the unpreserved samples (Sample UP01 and Sample UP02).

Similarly, there was a drop in S2 values, with the preserved samples averaging 9.3 mgHC/g (Sample 1, Sample 2, and Sample 3), and the unpreserved samples averaging 3.6 mgHC/g (Sample UP01 and Sample UP02). These changes represented a $\Delta 56\%$ drop in S1 values and a $\Delta 60\%$ drop in S2 values between preserved and unpreserved samples (Figure 4). The differences in thermal maturity values were minimal, with an average TMAX of 480 °C for preserved samples (Sample 1, Sample 2, and Sample 3) and an average TMAX of 472 °C for unpreserved samples (Sample UP01 and Sample UP02).

Core 2 results show also a slight drop in TOC values between preserved and non-preserved samples. The average TOC for Sample 1, Sample 2, and Sample 3 is 9.0 wt%. This value drops to 5.55 wt% (average value from UP01 & UP02) in the unpreserved sample. The change in TOC between preserved and unpreserved samples is around $\Delta 38\%$ (Figure 4).

Core 3 results show minor changes with negligible differences between preserved and un-preserved results with no major change in S1 values (Figure 5). The difference value from preserved samples is 8.1 mgHC/g, which is the average S1 for the four preserved samples. While UP01 and UP02 show a value of 8.85 mgHC/g and 7.14 mgHC/g. 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 15.0 mgHC/g (average S2 for the four preserved samples). While UP01 and UP02 show average values of 11.16 mgHC/g and 12.03 mgHC/g. In addition, results from preserved samples show a TMAX average value of 462°C (for the four preserved samples). While UP01 and UP02 show average values of 475.5°C and 472.7°C. Finally, Core 3 shows also a negligible change in TOC values between preserved and non-preserved samples. The average TOC for Sample 1, Sample 2, Sample 3 and Sample 4 (preserved samples) is 12.9 wt%, whereas TOC average values from UP01 and UP02 are 10.29 wt% and 13.59 wt%, respectively. 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 2).

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 (Figures 3, 4, and 5). Through the three cores, S1 values decline with a gradual dropping trend which reached to 87% out of the total S1 reported from preserved samples (Figures 3, 4, and 5). This variation in S1 losses can be correlated with thermal maturity variation. High thermal maturity cores (Core 1 and Core 2) report higher S1 drops (56%-87%) (Figures 3 and 4). On the other hand, Core 3 with a relatively less thermal maturity level shows few S1 losses (Figure 5). Furthermore, TOC variation seems to have no clear control over the S1 losses through the three cores (Table 1). The correlation between S1 losses and TOC was not proved during this comparison (Table 2).

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 (Figures 3, 4, and 5). 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 60-87% out of the total S2 values (Figures 3 and Figure 4). While the relatively low thermal maturity core (C3) reports a lower S2 drop (Figure 5). Similar to S1, this comparison couldn't prove the correlation between the S2 losses and organic richness (TOC) (Table 2).

TMAX values show an increasing trend with time through the three cores (Figure 3, Figure 4, and Figure 5). This change is reported in a very narrow range between 6-80C 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 2). TMAX 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 TMAX peak will inaccurately be picked through the lab instrument as the S2 peak is relatively lower in values with wider and broader 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 (Figures 3, 4, and 5). In high thermal maturity cores (C1 and C2) TOC results report a decline reported in preserved samples (Figures 3 and 4). While the low-maturity cores report less losses out of the total TOC (Figure 5). 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 2). 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).

Similarly, a 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 TMAX was reported with 2°C after 12 weeks.

Furthermore, 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, TMAX increased with 0-2°C with negligible fluctuation in TOC with a difference ranging from 0.03- 0.16%.

Implications of Sample Preservation and Storage on Source Rock Assessment

Core samples play a vital role in reservoir characterization, basin modeling, and geological studies. However, it is crucial to acknowledge the potential impact of poor core preservation and storage on the reliability of the results obtained from these studies. In particular, source rock evaluation and resource assessment through pyrolysis analysis can be significantly affected by the loss of free hydrocarbons (S1) and the release of gases during inadequate sample preservation.

One of the key diagnostic parameters for assessing moveable hydrocarbon content in shale oil is the oil saturation index (OSI), as proposed by Jarvie (2012). This index relies on the measurement of free hydrocarbons in the rock, represented by S1 values obtained through Rock-Eval pyrolysis. However, it is important to recognize that there can be a significant discrepancy between the measured S1 value and the true in-situ value underground. This disparity becomes more pronounced as the gas content increases (Xianzheng, 2021).

The non-representative S1 values resulting from losses and inadequate preservation can be misleading when using pyrolysis proxies to identify subsurface potential. This issue is particularly relevant in unconventional rocks, where the determination of the volume of oil present depends on the measurement of the free hydrocarbon portion. In cases of shale formations saturated with liquid hydrocarbons, direct geochemical measurements of hydrocarbons contained in rock samples collected from liquid-rich shale intervals can help assess oil-in-place. However, it is imperative to consider the credibility of any resource or reserve assessment method.

One significant challenge in preserving core samples is the evaporation of light compounds and light liquid hydrocarbons during the handling procedures at the surface. This evaporation, whether partial or complete, can lead to inaccurate measurements and potentially compromise the representativeness of the core sample.

In addition to the points mentioned above, it is important to note that traditional resource estimates often overlook the loss of gaseous oil due to evaporation during coring. This issue has been highlighted by Li et al. (2020). To accurately estimate in-place oil reserves, it is necessary to incorporate correction factors that account for evaporative losses. These correction coefficients depend on the API gravity of the oil and the maturity level of the shale rock (Sowizdzal, 2020).

It should be noted that estimations based solely on S1 values can lead to significant underestimations, as the S1 parameter only reflects a portion of the original hydrocarbon compounds present in the shale rock under reservoir conditions (Sowizdzal, 2020). Therefore, laboratory analytical procedures have been developed to determine correction coefficients and enable proper adjustment.

Abrams et al. (2017) emphasized the importance of correcting for evaporative loss in resource evaluation by introducing the term $S1_{Loss}$ in the total oil yield equation. The estimation of S1 loss can be achieved by determining the density of the hydrocarbon fluid in place, which can be obtained from gas chromatography of the whole oil extract or estimated using relationships based on biomarker compounds (Michael et al., 2013).

Moreover, Guo (2020) proposed a calculation method for the evaporative hydrocarbon recovery coefficient based on the formation volume factor. This method allows for the calculation of the original quantity of underground shale oil by considering the viscosity and density of the subsurface oil. Similarly, the quantity of surface shale oil can be determined by multiplying the surface oil density with its viscosity at 50°C. By applying Equation 1, the dimensionless evaporative hydrocarbon recovery coefficient (k_{S1}) can be estimated. It is important to note that Q_{or} represents the original quantity of underground shale oil in tonnes, Q_{pd} represents the quantity of surface shale oil in tonnes, V_{sub} represents the volume of underground shale oil in cubic meters, V_{pd} represents the volume of surface shale oil in cubic meters, B_o represents the dimensionless crude oil volume factor, ρ_{sub} represents the density of formation oil in tonnes per cubic meter, and ρ_{pd} represents the density of surface oil in tonnes per cubic meter.

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

Conclusion

In conclusion, good preservation of core samples 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 obtained from this study 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 TMAX show very minor changes that are interpreted as a result of the lateral heterogeneity in the 1-foot core. 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 show a significant drop over time (Figures 3-5). 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, TMAX was also affected by the change in S1 and S2 values with a slight increase in TMAX values (Figure 3, Figure 4, and Figure 5). 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 drop by up to 87% over the observation time interval, while TOC measurements showed a drop that reached 62%.
- The slight increase in TMAX 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 TMAX 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 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 and 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.

Figure Captions

Figure 1: Example of 1 foot of conventional core used during this study. A & B: the core conditions when it was opened. The core was completely covered by wax layers. C: Samples after removing the wax That is underlain by two more layers of aluminum foil and plastic wrap.

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.

Figure 3: Comparisons between results obtained from preserved and un-preserved core samples for Core 1. Results from un-preserved 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, TMAX values were also affected by preservation due to changes in S1 and S2 values. C1-UP01 & C1-UP02 are two un-preserved samples from Core 1, while Sample 1, Sample 2 and Sample 3 are preserved samples from Core 1. For confidently; values were adjusted with constant factor.

Figure 4: 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, TMAX values were also affected by preservation due to changes in S1 and S2 values. C1-UP01 & C1-UP02 are two un-preserved samples from Core 2, while Sample 2, Sample 3 and Sample 4 are preserved samples from Core 2. For confidently; values were adjusted with constant factor.

Figure 5: 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, TMAX, and TOC values. C1-UP01 & C1-UP02 are two un-preserved samples from Core 3, while Sample 1, Sample 2, Sample 3 and Sample 4 are preserved samples from Core 3. For confidently; values were adjusted with constant factor.

Table Captions

Table 1: 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. For confidently; values were adjusted with constant factor.

Table 2: Summary of pyrolysis changes related to the variations in thermal maturity and organic richness in the three study cores. For confidently; values were adjusted with constant factor.

Figures

Figure 1:

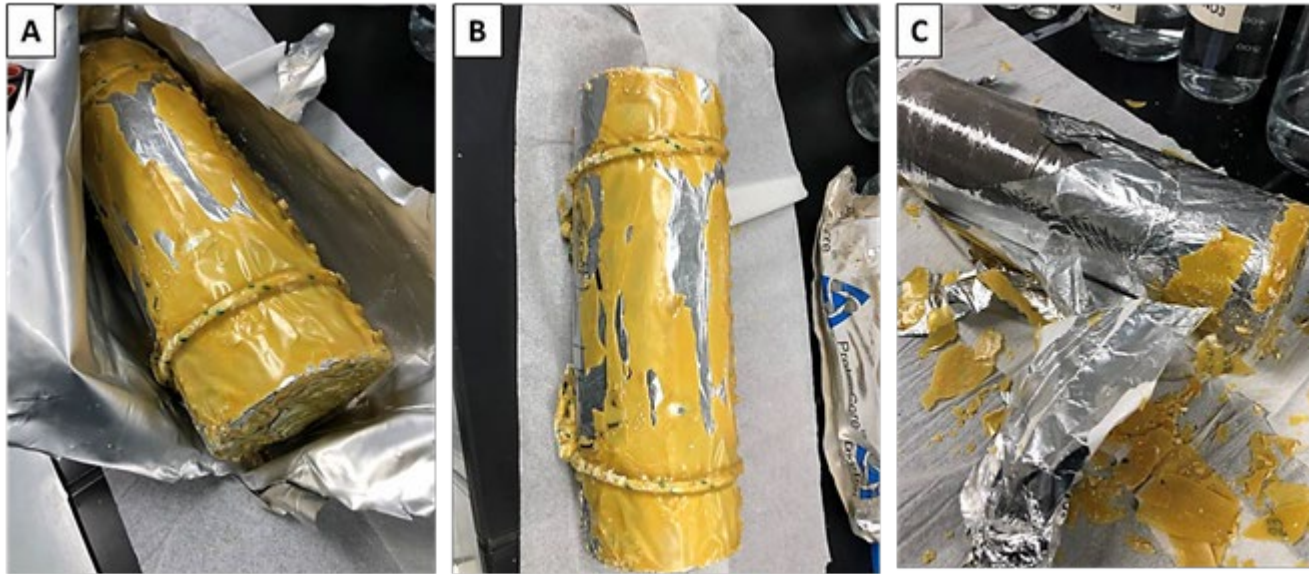


Figure 2:

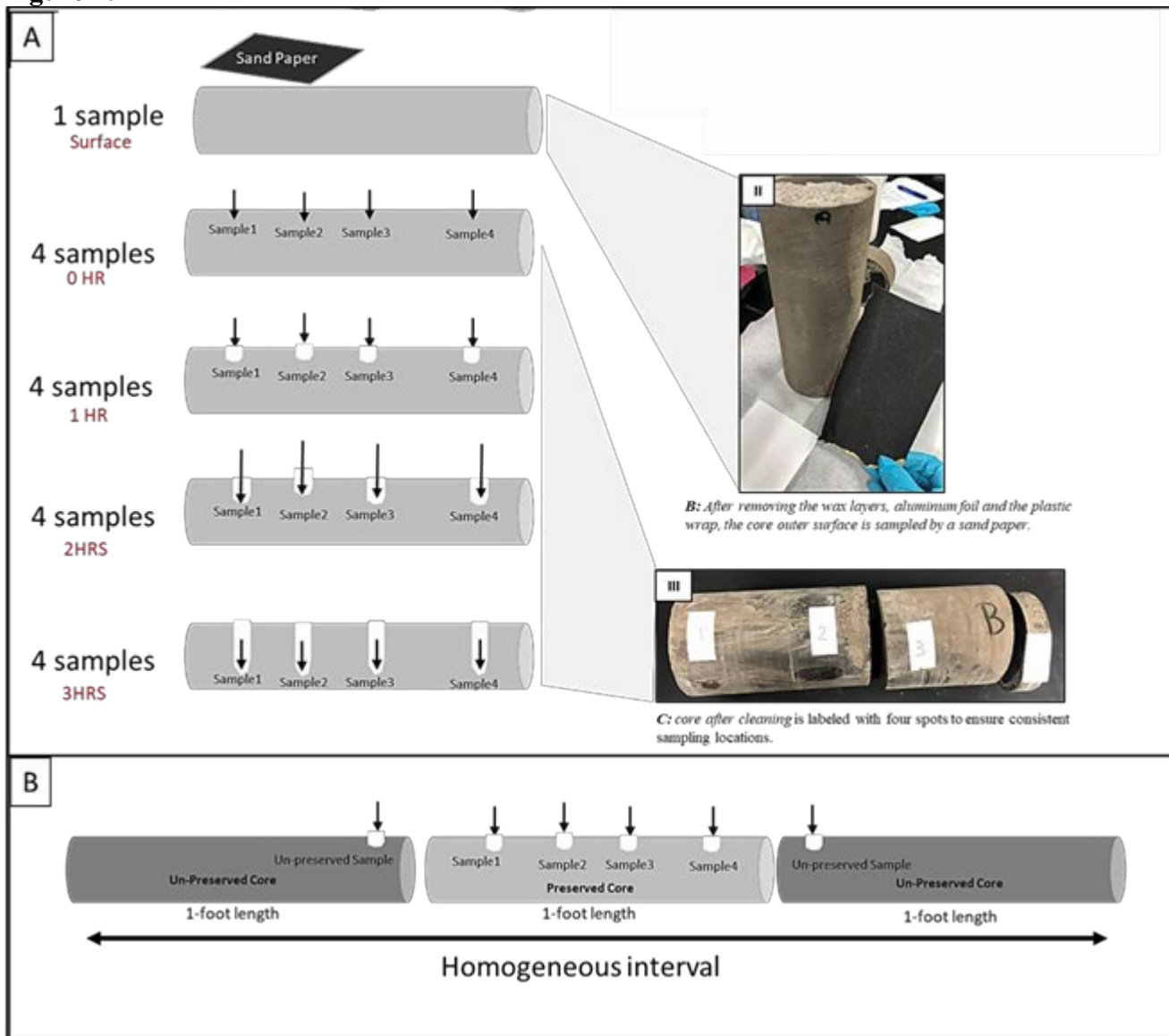


Figure 3:



Figure 4:



Figure 5:



Tables

Table 1:

| Well ID | Core ID | Organic Richness (TOC%) | Thermal Maturity (T_{MAX}) |
|----------------|----------------|--------------------------------|---|
| Well 1 | 1 | 12.0 – 30.0 | 470-475 |
| Well 1 | 2 | 6.0 – 12.0 | 470-475 |
| Well 2 | 3 | 9.0 -18.0 | 460-465 |

Table 2:

| Core ID | Relative Organic Richness | Relative Thermal Maturity | Δ S1% | Δ S2% | Δ T_{MAX} °C | Δ TOC% |
|----------------|----------------------------------|----------------------------------|--------------|--------------|-----------------------------|---------------|
| C1 | High (24.0 wt% TOC) | High (470-475°C) | 59 | 58 | 8.0 | 54 |
| | Med (10.5 wt% TOC) | High (470-475°C) | 87 | 87 | 6.0 | 62 |
| C2 | Med (9.0 wt% TOC) | High (470-475°C) | 56 | 60 | 8.0 | 38 |
| C3 | Med (13.5 wt% TOC) | Low (460-455°C) | <40 | <40 | >7.0 | <30 |

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