

**[CO₂-CARBONATE MUDROCK INTERACTIONS:
INVESTIGATING THE INFLUENCE OF ORGANIC
RICHNESS AND MATURITY VARIATIONS THROUGH
STABLE ISOTOPIC, GEOCHEMICAL AND
PETROPHYSICAL ANALYSIS]**

BY

RAJAI ABDULLAH AL HUBAIL

A Thesis Presented to the
**COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS**

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

GEOLOGY

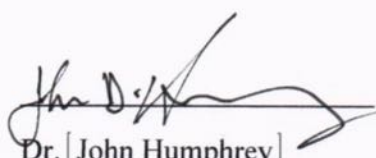
January 2025

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

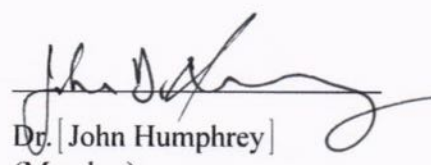
This thesis, written by **Rajai Abdullah Al Hubail** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN GEOLOGY**.


Dr. [John Humphrey]
Department Chairman


Dr. Suliman Al-Homidan
Dean of Graduate Studies

01/20/2025
Date


Dr. [Israa Abu Mahfouz]
(Advisor)


Dr. [John Humphrey]
(Member)


Dr. [Ammar Elhusseiny]
(Member)



© Rajai A. Al Hubail

2025

[This work is happily dedicated to my mother, my wife, my family, and my close friends, whose unwavering support, belief in my abilities, and continuous encouragement have been the foundation of my strength throughout this journey.

I also dedicate this work to the loving memory of my father, who passed away when I was still young. Although he is no longer with us, his values, guidance, and spirit have remained a source of inspiration in our lives and accomplishments.]

ACKNOWLEDGMENTS

[First and foremost, I would like to express my deepest gratitude to **my mother, my wife,** and **my family** for the continuous support and belief in my abilities, and encouragement throughout this journey. Without your support, this achievement would not have been possible.

I am also grateful to my advisor, **Dr. Israa** whose guidance, persistence, and encouragement pushed me to complete this work in such a short period of time. Your support at every step, from prioritizing my ideas to finalizing this thesis, has been invaluable.

I would also like to thank my committee members, **Dr. John** and **Dr. Ammar** for their valuable feedback, and continuous support, which have greatly enhanced the quality of this work.

Finally, a special thank you to **Dr. Amjed**, who stood by me from the very first day of the experiment. Your patience, expertise, dedication, and constant motivation played a critical role in bringing this research alive.

To everyone who contributed to this journey, thank you for being a part of it]

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES.....	IX
LIST OF FIGURES.....	X
LIST OF ABBREVIATIONS.....	XII
ABSTRACT.....	XIII
ملخص الرسالة.....	XIV
CHAPTER 1 INTRODUCTION.....	1
1.1 Background	1
1.2 Problem Statement	3
1.3 Objectives and Research Questions	4
CHAPTER 2 LITERATURE REVIEW.....	5
2.1 Carbonate Mudrock Source Rock.....	5
2.2 Source Rock Organic Richness and Maturity	6
2.2.1 Organic Matter Primary Productivity and Preservation.....	8
2.3 Petrophysical and Mechanical Properties	9
2.3.1 Pore Geometry and Distribution	9
2.3.2 Acoustic Methods for Elastic Property Characterization.....	10
2.4 CO ₂ Sequestration in Unconventional Hydrocarbon Reservoirs.....	11
2.5 Isotope Geochemistry	14
2.5.1 Carbon, Oxygen and Sulfur.....	14
2.5.2 Stable Isotope Analysis.....	15
CHAPTER 3 GEOLOGICAL SETTINGS	18

CHAPTER 4 METHODOLOGY	21
4.1 Sample Selection and Preparation.....	21
4.2 CO₂ Treatment Workflows.....	21
4.2.1 Powdered Sample CO ₂ Treatment Workflow	21
4.2.2 Core Sample CO ₂ Treatment Workflow	22
4.3 Analytical Techniques	23
4.3.1 Geochemical Analysis.....	23
4.3.2 Petrophysical Analysis.....	24
4.3.3 Microscopic Imaging	25
CHAPTER 5 RESULTS.....	26
5.1 Geochemical analysis	28
5.1.1 Mineralogical Composition	28
5.1.2 Elemental Composition	29
5.1.3 Pyrolysis Analysis	31
5.1.4 Isotope Analysis	33
5.2 Petrophysical Analysis.....	35
5.2.1 VP/VS Results	35
5.2.2 NMR Results.....	36
5.2.3 Dielectric Results.....	42
5.3 SEM Images	45
5.3.1 JS Samples	45
5.3.2 EF samples.....	47
5.4 CT Scan	49
CHAPTER 6 DISCUSSION.....	55
6.1 Pre CO₂-Treatment Sample Characterization	56
6.2 Post CO₂-Treatment Characterization.....	58
6.2.1 Petrophysical Analysis.....	58
6.2.2 Geochemical Analysis.....	61
6.3 Influence of Organic Richness and Maturity Variations on Stable Isotope Ratios for pre- and post- CO₂-Treated Samples.....	62
6.3.1 Sulfur Isotope Ratios	62
6.3.2 Carbon Isotope Ratios	62
6.3.3 Oxygen Isotope Ratios	63
6.3.4 Stable Isotope Fractionation	64

CHAPTER 7 CONCLUSION.....	66
REFERENCES	I
VITAE.....	V

LIST OF TABLES

Table 1. Mineralogical data for pre- and post-CO ₂ treatment Powdered Samples	28
Table 2. Elemental data for pre- and post-CO ₂ treatment Powdered Samples	30
Table 3. Pyrolysis Data for Immature and Mature Samples	32
Table 4. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ isotope data for all stages of the immature and mature samples	34
Table 5. Vp/Vs Values of JS and EF samples for all stages	35

LIST OF FIGURES

Figure 1. Worldwide mineralogical comparison of Carbonate Mudrocks along with JS and EF of this study Modified after (Usman et al., 2024).	6
Figure 2. Alignment of Atomic Elements Under Electrical Current Induction (Dielectric Permittivity — GPG 0.0.1 Documentation)	10
Figure 3. A competitive adsorption of CO ₂ -CH ₄ and CH ₄ desorption in shale (Wang et al., 2024 and Lu et al., 2022).	12
Figure 4. A schematic diagram showing from a to c; natural and newly formed fractures, CO ₂ movement in organic matter, oil desorption and forming of CO ₂ wet shale, and finally oil and CO ₂ flowing in the fractures due to pressure reduction (from Wang et al., 2024).....	13
Figure 5. Different shale formation minerals reactions with CO ₂ (Hazarika et al., 2023)	13
Figure 6. Central and southern Jordan stratigraphic column of the Upper Cretaceous strata (Abu-Mahfouz et al., 2022).....	19
Figure 7. Contoured maps showing TOC wt. % and clay content of Lower Eagle ford shale (Hou et al., 2021).....	20
Figure 8. Eagle ford stratigraphic column along with well log for the same interval (Ratcliffe et al., 2012).....	20
Figure 9. The workflow followed for the analysis of the powdered samples.....	25
Figure 10. The workflow followed for the analysis of the core plugs.....	25
Figure 11. CO ₂ Treatment Conditions for both the powdered and core sample.....	25
Figure 12. Overview of types of samples and analysis results data.....	27
Figure 13. Mineralogical Composition plot for pre- and post-CO ₂ treatment powdered Samples.....	29
Figure 14. Elemental Composition plot for pre- and post-CO ₂ treatment powdered samples	31
Figure 15. Pyrolysis plot for Immature and Mature samples, Mature Samples exceed the plot limits	32
Figure 16. NMR results for all stages of the JS sample.....	37
Figure 17. NMR results for all stages of EF sample.....	37
Figure 18. Dielectric Permittivity Data for JS sample.....	43
Figure 19. Dielectric Conductivity Data for JS sample	43
Figure 20. Dielectric Permittivity Data for EF sample	44
Figure 21. Dielectric Permittivity Data for EF sample	44
Figure 22. SEM Images for the initial pre-treated stage of JS.....	45
Figure 23. SEM Images for the post CO ₂ -treated stage of JS core side showing possible microstructure and pore enhancement	46
Figure 24. SEM Images for post CO ₂ -treated stage of JS core center showing diagenetic overprinting.....	46

Figure 25. SEM Images for initial pre-treated stage of EF showing a foraminifera foram	47
Figure 26. SEM Images for initial pre-treated stage of EF showing microstructures and pores distribution	47
Figure 27. SEM for post CO ₂ -treated stage of EF core side showing diagenetic overprinting such as reprecipitation.....	48
Figure 28. SEM for post CO ₂ -treated stage of EF core center showing possible microstructure and pores enhancement.....	48
Figure 29. CT scan images of untreated JS sister sample.....	50
Figure 30. CT scan images of CO ₂ -treated JS sample	50
Figure 31. CT scan images of JS samples; non-treated sister sample (top) and CO ₂ -treated sample (Bottom).....	51
Figure 32. CT scan images of untreated EF sister sample	52
Figure 33. CT scan images of CO ₂ -treated EF sample	53
Figure 34. CT scan images of EF samples; non-treated sister sample (Top) and CO ₂ -treated sample (Bottom).....	54
Figure 35. Dissolution and precipitation processes during CO ₂ injection (Li et al. 2022), which agrees with the thesis SEM results from Figures 24 and 27	61
Figure 36. Plot for d13C (‰VPDB) vs. d18O (‰VPDB) isotopes for all samples showing the shift differences between both samples as well as their maturity stage. it is well noticed that Immature JS-LB scores the biggest carbon isotope shift	63
Figure 37. An illustration of variable chemical formula for each kerogen types (Sun et al., 2023).	64

LIST OF ABBREVIATIONS

Carbon dioxide (CO ₂)	Upper Cretaceous Muwaqqar Chalk Marl Formation (MCM)
UN Climate Change Conference (COP21)	X-Ray Diffraction Analysis (XRD)
Carbon Capture, Utilization, And Storage (CCUS)	X-Ray Fluorescence Analysis (XRF)
Enhanced Oil Recovery (EOR)	Gas Chromatography Isotope Ratio Mass Spectrometry Instrument (GC-IRMS)
Jordanian Shale (JS)	Vienna PeeDee Belemnite (VPDB)
Eagle Ford Shale (EF)	Vienna Standard Mean Ocean Water (VSMOW)
Total Organic Carbon (TOC)	Vienna Canyon Diablo Troilite (VCDT)
Methane (CH ₄)	Scanning Electron Microscopy (SEM)
Water (H ₂ O)	Powdered Pre-CO ₂ treatment (-Pre)
Organic Matter (OM)	Powdered Post-CO ₂ treatment liquid brine samples (-LB)
Sediments Water Interface (SWI)	Powdered Post-CO ₂ treatment dry samples (-dry)
Nuclear Magnetic Resonance (NMR)	Hydrocarbon (HC)
Compressional Wave Velocity (V _p)	Amount of Free Hydrocarbon (S1)
Shear Wave Velocity (V _s)	HC Generated by Thermal Cracking (S2)
Carbon Isotope (¹³ C)	Temperature at S2 Peak (Tmax)
Oxygen Isotope (¹⁸ O)	Potassium Chloride (KCl)
Sulfur Isotope (³⁴ S)	Dissolved Inorganic Carbon (δ ¹³ C _{DIC})

ABSTRACT

Full Name : [Rajai A. Al-Hubail]

Thesis Title : [CO₂-Carbonate Mudrock Interactions: Investigating the Influence of Organic Richness and Maturity Variations Through Stable Isotopic, Geochemical and Petrophysical Analysis]

Major Field : [Geology]

Date of Degree : [January 2025]

This thesis aims to investigate the effects of CO₂ treatment on carbonate mudrock source rock samples. The main objectives of the study are (a) to investigate the influence of organic richness and maturity variations on the stable isotopic responses, and (b) to investigate geochemical, geomechanical, and petrophysical properties of carbonate mudrock after treatment with CO₂. The carbonate mudrock samples used in this study are geographically different; one was collected from the Upper Cretaceous carbonate mudrock strata in Jordan, and the other one is from the Eagle Ford Formation, US. The Jordanian sample is richer in organic matter but less mature compared to the Eagle Ford sample. Compositionally, the Eagle Ford sample has more calcite than the Jordanian shale sample. The effect of CO₂ treatment was examined through sequential sets of petrophysical experiments, and geochemical analysis complemented with SEM (Scanning Electron Microscope) imaging and computed tomography (CT) scan. The analysis has been conducted at different stages on powdered and core samples, sequentially. For core analyses, the workflow started with a dry initial stage followed by a brine-saturated stage and ended with a CO₂-treated stage. For powdered samples, they were divided into two types: dry and wet/ immersed in 3% potassium chloride (KCl) liquid brine. The petrophysical analyses included the compressional and shear velocities, electrical analysis as in permittivity and conductivity, and Nuclear Magnetic Resonance (NMR). These analyses have concluded that there has been enhancement of the pore system and its connectivity in the samples, through either dissolution or fracturing. Moreover, JS and EF isotope results reveal that different isotopes shifted differently with the CO₂ dry and liquid brine treatment. Those isotope shifts are interpreted to be due to different organic matter richness, thermal maturity, and diageneses processes that the source rock has undergone. Finally, mineral dissolution and mineral reprecipitation are interpreted by inorganic geochemical analysis, which agrees with SEM as it was represented by pore size enhancement with an indication of mineral reprecipitation.

ملخص الرسالة

الاسم الكامل: رجائي عبد الله آل حبيب

عنوان الرسالة: تفاعلات ثاني أكسيد الكربون مع الصخور الرسوبية: تحقيق في تأثير الثراء العضوي واختلافات النضج من خلال قراءة النظائر المستقرة، التحاليل الجيوكيميائية والبتروفيزيائية

التخصص: جيولوجيا

تاريخ الدرجة العلمية: رجب ١٤٤٦ |

تهدف هذه الأطروحة إلى دراسة تأثير معالجة ثاني أكسيد الكربون على بعض عينات الصخور الرسوبية. الأهداف الرئيسية للدراسة هي (أ) دراسة تأثير ثراء المواد العضوية واختلاف النضج لصخور المكن على الاستجابة للنظائر المستقرة، و (ب) دراسة الخصائص الجيوكيميائية والجيوميكانية البتروفيزيائية للصخور الطينية الكربونية بعد المعالجة بثاني أكسيد الكربون. تختلف عينات صخور المكن الطينية المنتقاة جغرافياً حيث إن إحداها من الأردن والأخرى من الولايات المتحدة الأمريكية. الصخر الأردني أكثر ثراءً بالمواد العضوية، ولكنه أقل نضجاً من الصخر الأمريكي. من ناحية التركيب الكيميائية، يحتوي الصخر الأمريكي على كالكسيت أكثر من الصخر الأردني. تم فحص تأثير معالجة ثاني أكسيد الكربون من خلال مجموعات متسلسلة من التجارب البتروفيزيائية وتحليل النظائر المستقرة والتحليل الجيوكيميائية غير العضوية وتم استكمال النتائج باستخدام التصوير المجهر الإلكتروني والتصوير المقطعي المحوسب. تم إجراء التحليل على مراحل مختلفة بشكل متسلسل على عينات باوذر مسحوقة وعينات مكتملة مستخرجة من باطن الأرض أثناء الحفر. بدءاً من تحاليل العينات المكتملة، كانت خطوات التجربة هي المرحلة الأولية الجافة تليها مرحلة مشبعة بالمحلول الملحي المائي وانتهاءً بمرحلة المعالجة بثاني أكسيد الكربون. أما بالنسبة لعينات الباوذر المسحوقة، تم تقسيمها إلى نوعين: أما جافة ومغمورة في محلول ملحي سائل. تضمنت التحليلات البتروفيزيائية سرعات الضغط (Vp/Vs) والتحليل الكهربائي (Dielectric) والرنين المغناطيسي النووي (NMR) وبينت التحليلات في معظم العينات إلى أنه هناك زيادة وتعزيز للمسام في الصخرة واتصالهم من خلال الذوبان للمعادن مع ملاحظة ظهور ترسيبات حول المعادن شوهدت باستخدام التصوير المقطعي المحوسب. علاوة على ذلك، كشفت نتائج النظائر أن النظائر المختلفة في أغلب العينات تفاعلت بشكل مختلف مع معالجة ثاني أكسيد الكربون بالمحلول الملحي أو بدونه. تُفسر الاستجابات المختلفة للنظائر المستقرة على أنها ترجع إلى الثراء العضوي المختلف وكذلك أنواع المواد العضوية والنضج الحراري للصخور والتأثيرات ما بعد الترسيب التي خضعت لها كلتا صخور المصدر. أخيراً، يوضح التحليل الجيوكيميائية غير العضوي لكلتا العينيتين تعزيز حجم المسام من خلال ذوبان بعض المواد بسبب التفاعل الكيميائي بين الصخر وثاني أكسيد الكربون مع الإشارة إلى إعادة ترسيب المعادن والذي يتفق مع المجهر الإلكتروني.

CHAPTER 1

INTRODUCTION

1.1 Background

The increasing urgency of addressing climate change has propelled carbon dioxide (CO₂) sequestration to the forefront of scientific and political discussions over the past three decades. The interest has drastically increased with the agreement to achieve net zero CO₂ emissions by 2050 in Paris, 2015, at the UN Climate Change Conference (COP21). Since then, sustainability technologies, including carbon capture, utilization, and storage (CCUS), have become a major mutual research interest for both academia and industry, where they are tackled from scientific and engineering perspectives. In response to the challenge of fulfilling the agreement and the rising concentration of CO₂ in the atmosphere, which is mainly driven by industrial activities and fossil fuel consumption, CO₂ sequestration is becoming a promising avenue.

Currently, a variety of CO₂ sequestration methodologies are under investigation, focusing on the effective capture and secure storage of this greenhouse gas. Key approaches include geological and biological methods, such as injecting CO₂ into soil, and geological methods, such as injecting CO₂ into geological formations and open deep saline aquifers ([Kalam et al., 2021](#); [Izadpanahi et al., 2024](#)). In some cases, the stored CO₂ undergoes mineralization and chemical reactions within these formations, ending up with permanent storage. Another method is the technological method which involves injecting CO₂ into oil and gas reservoirs for enhanced oil recovery (EOR).

Among the various geological formations suited for CO₂ storage, unconventional hydrocarbon formations are becoming a promising option. Their widespread availability and substantial potential storage capacity make them an attractive target for CO₂ geological sequestration ([Kalam et al., 2021](#)). However, sequestering CO₂ within these rocks introduces a complex, multi-scale phenomenon that encompasses spatial dynamics ranging from the nanoscale to the kilometer scale ([Wang et al., 2023](#)).

This complexity necessitates an in-depth understanding of the geochemical and petrophysical interactions that govern the behavior of CO₂ in these formations.

This thesis study will focus on the geochemistry and petrophysics of geological CO₂ sequestration, as these disciplines are integral to multiple stages of geological CO₂ sequestration. Geochemical and physical processes such as absorption and adsorption of CO₂, dissolution, and precipitation of minerals within the targeted reservoirs are explored. Importantly, the thesis examines how alterations in the properties of minerals may influence fluid dynamics and capillary trapping mechanisms. Importantly, the thesis will investigate how high-rate CO₂ injection can potentially open existing fractures or generate new ones, further complicating the sequestration landscape. By advancing our understanding of these interactions, this work seeks to contribute valuable insights into optimizing CO₂ sequestration efforts and addressing the pressing challenges of climate change.

1.2 Problem Statement

Understanding the characteristics of supercritical carbon dioxide (CO₂) is widely regarded as a crucial element in predicting its behavior within subsurface environments, as well as in effectively monitoring carbon sequestration systems and sites ([Rosso, 2013](#); [Kalam et al., 2021](#)). Despite this acknowledgment, there remains significant potential for enhancement in the monitoring processes associated with the behavior of sequestered CO₂. The literature reviewed on this topic reveals that discussions are primarily divided into two main sections. The first part focuses on the implications of CO₂ sequestration in shale formations, addressing aspects from geochemical, geomechanical, and petrophysical perspectives (e.g., [Kalam et al., 2021](#); [Sun et al., 2023](#)). This thorough examination helps in understanding how these factors interact with CO₂ storage and the overall integrity of the geological formations involved.

The second part of the literature delves into the isotopic shifts of carbon and oxygen within deep saline aquifers, as well as investigations conducted in laboratory settings involving brine. It explores current monitoring techniques employed in CO₂ sequestration, emphasizing the interactions occurring between CO₂, water, and rock (e.g., [Humez et al., 2014](#)). However, a notable gap in the existing literature is the lack of discussion surrounding the application of isotopic responses specifically in sequestered shale formations. This oversight presents an opportunity for further research in a critical area of carbon capture and storage.

A review of isotope geochemistry literature indicates that the degree of fractionation between two isotopes of the same element is significantly influenced by their respective masses and the temperature of their surrounding environment. Variations in the isotopic composition of elements can provide valuable insights into the physical, geochemical, and biogeological processes that have shaped the characteristics of the rock material involved ([Faure & Mensing, 2005](#)).

Therefore, there is an urgent need to explore the utilization of isotopic responses in sequestered shale formations to advance our understanding and monitoring of CO₂ sequestration. By bridging this gap, we can enhance the accuracy of forecasts regarding CO₂ behavior in subsurface systems and improve the efficacy of monitoring techniques, ultimately contributing to more effective and sustainable carbon management strategies.

1.3 Objectives and Research Questions

The main aim of this thesis study is to investigate the effect of CO₂ treatment on carbonate mudrock source rocks and to answer whether isotopic signatures can be used as indicators of CO₂ sequestration in carbonate mudrock formations. The objectives of the study are (a) to investigate the influence of organic richness and maturity variations on the stable isotopic responses, and (b) to investigate geochemical, geomechanical, and petrophysical properties of carbonate mudrock after treatment with CO₂.

This study mainly aims to address the following research questions:

- 1- What is the influence of source rock organic richness and maturity variations on the stable isotopic responses before and after CO₂ treatment?
- 2- What are the possible geochemical, geomechanical, and petrophysical property changes of carbonate mudrock after CO₂ treatment?

[CHAPTER 2]

LITERATURE REVIEW

2.1 Carbonate Mudrock Source Rock

Carbonate mudrocks are well known for their inorganic and organic geochemical heterogeneities, as well as their varying maturity levels. They span from calcium-rich to silica-rich, organic-rich to organic-lean and immature to mature. Such heterogeneities make the interest in understanding each type of carbonate mudrocks and their significance in terms of their chemical and physical behavior when treated with CO₂. Figure 1 shows the inorganic compositional heterogeneities across major mudrocks worldwide.

In this thesis study, two compositionally distinct carbonate mudrock samples were chosen to conduct the experiment; one from the Upper Cretaceous (Maastrichtian) Jordanian carbonate mudrocks, also known as the Jordan Oil Shale (JS), and the other from the Eagle Ford (EF) carbonate mudrock.

Another crucial heterogeneity that is mentioned in literature is the geomechanical heterogeneity of carbonate mudrocks due to their different mineralogical compositions. Some tend to be more fissile and easily develop internal fractures when treated with CO₂ while others reveal more intact internal with less effect after the treatment. [Yang et al. \(2019\)](#) discussed this heterogeneity and linked it with the complexities of the pore-grain and pore network of the carbonate mudrocks, varying from nano-size to multi-scale pore throats, as well as their capability of adsorption and absorption depending on their organic matter richness. Thus, when total organic carbon (TOC) is low, the effect will be mainly controlled by the geochemical

composition of the inorganic pores. Moreover, the fluid flow in carbonate mudrock is controlled by the spatial distribution and spatial relationship between organic and inorganic matter within the rock. Which is suggested to be divided into three types: dense continuous distribution, sparse continuous distribution, and discontinuous distribution. Adding to this the dynamic effects in the subsurface which are temperature and pressure.

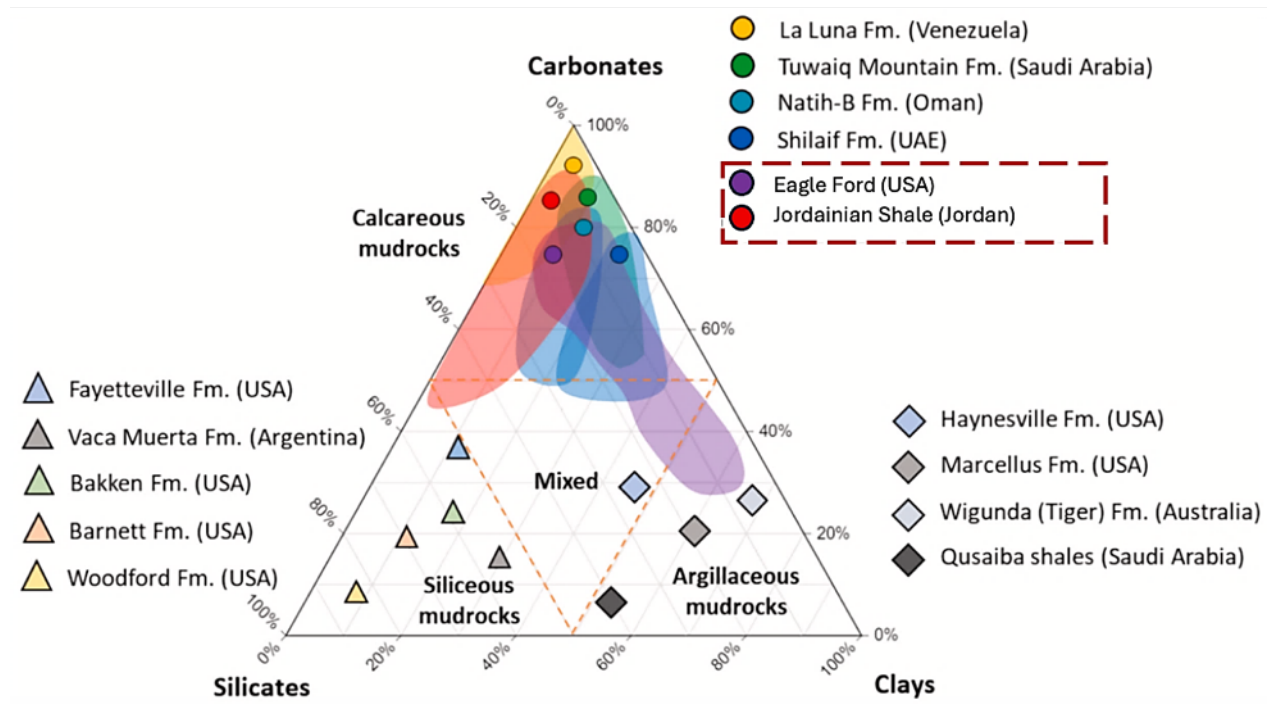


Figure 1. Worldwide mineralogical comparison of Carbonate Mudrocks along with JS and EF of this study Modified after (Usman et al., 2024).

2.2 Source Rock Organic Richness and Maturity

As organic matter sinks in aquatic basins, it accumulates within the sediments and gets buried over time. Within time, and because of the burial effect and geothermal gradient increase, organic-rich sediments experience a series of alterations divided into three phases: diageneses, catagenesis and metagenesis (Selley & Sonnenberg, 2014).

Initially, diagenesis takes place in shallow subsurface under regular temperature and pressure. Throughout this stage, organic matter releases methane (CH_4), carbon dioxide (CO_2), and water (H_2O), leaving behind a complex hydrocarbon termed kerogen, which releases petroleum when heated. Mainly kerogen types represent the deposition environment as kerogen type I represents mainly lacustrine deposition environment, whereas kerogen type II is mainly deposited in marine environments and type III is terrestrial. Finally, kerogen type IV suggests reworked sediments from older sedimentary formations.

As the burial depth increases, diagenesis evolves into catagenesis by an increase in temperature. Catagenesis is the primary phase in the early maturation of petroleum formation as oil onset is at 120°C . Different kerogen types mature differently with the heat increment. Further burial and temperature increase lead to metagenesis at around 200°C . In this final stage, the residual kerogen slowly decomposes, resulting in the breakup of the lighter hydrocarbon molecules to pure carbon.

2.2.1 Organic Matter Primary Productivity and Preservation

In marine sediments, the most popular organic matter (OM) is phytoplankton which consists of Proteins, carbohydrates, and lipids. Nevertheless, terrigenous OM can be found in marine sediments which could be drifted away by rivers or wind and could be dissolved or not ([ABOUSSOU, 2016](#)). Usually, bacteria and animals degrade the OM, and nutrients exist in the water column at the time of precipitation, hence the interest in understanding the relationship between organic carbon burial and environmental factors that govern the deposition. For instance, oxic, sub-oxic, and anoxic water will have their bacteria that degrade oxygen, manganese, iron, and sulfur depending on their existence. The deeper the organic matter sinks in the sediments water interface (SWI), the more of a shifting reaction will be from aerobic to anaerobic bacteria where they will need less oxygen, and several redox occurs such as sulfate reduction below the ferruginous zone (stratified layers of different metabolic niches) ([Konhauser, 2007](#)). However, different environments will change the redox condition, for instance, restricted basins will have different conditions than in open marine basins in terms of the chemocline (Oxic to Anoxic level). Organic matter fluxes, rain, sea-level fluctuation, and sedimentation rate are common factors in primary OM productivity and preservation. In restricted basins yet with sea level fluctuation, oxygenated water (fresh fluxes) will mix with the bottom non-oxygenated water, and the bottom nutrient will climb up in the water column and might end up with mixed chemicals within the water.

2.3 Petrophysical and Mechanical Properties

2.3.1 Pore Geometry and Distribution

The importance of understanding pore structures and their evolution in shale formations has grown significantly with the increasing focus on carbon dioxide (CO₂) sequestration in shale reservoirs. Their low permeability and high organic content, present both opportunities and challenges for CO₂ sequestration. Precise characterization of shale's pore structure is essential to optimize CO₂ storage and ensure long-term containment.

Dielectric permittivity is a key parameter that can provide insights into pore size and distribution within shale rocks. This property measures a material's ability to store electrical energy in an electric field, as it is influenced by the type and distribution of fluids within the pore spaces. Dielectric permittivity is a measure of how a material responds to an electric field and how it affects the electric field within the material. It quantifies the material's ability to polarize in response to the field. Permittivity is a fundamental property that describes how much electric field (or flux) can be "permitted" to pass through a material. Different materials have different permittivity, reflecting their molecular structure and the ability of their molecules to polarize. Alongside dielectric permittivity, Nuclear Magnetic Resonance (NMR) can offer detailed information about the distribution and mobility of fluids, enhancing the understanding of fluid-rock interactions. Finally, Electrical conductivity in rocks is an important parameter that provides insight into the composition, fluid content, and connectivity of pore spaces within the rock matrix ([Hassan et al., 2024](#)).

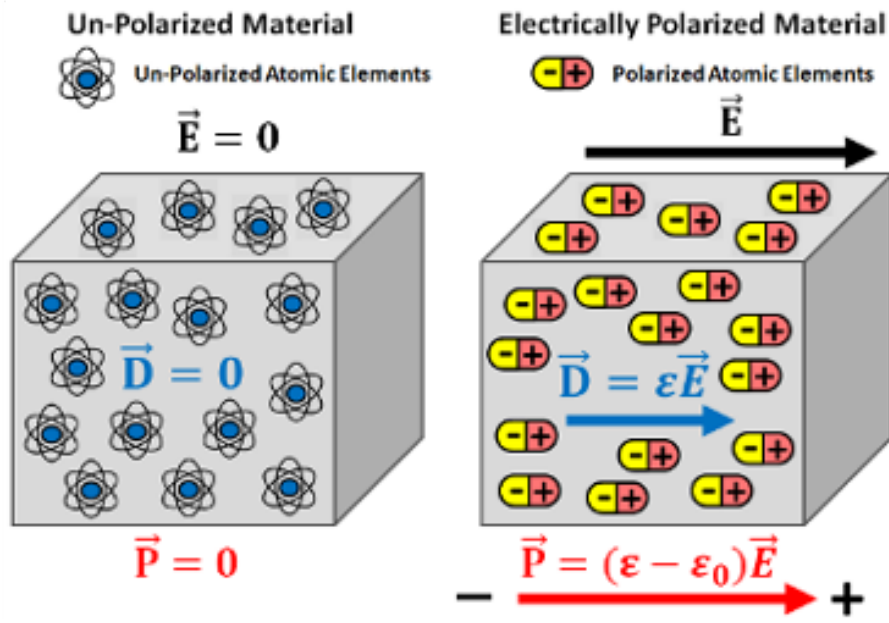


Figure 2. Alignment of Atomic Elements Under Electrical Current Induction (Dielectric Permittivity — GPG 0.0.1 Documentation)

2.3.2 Acoustic Methods for Elastic Property Characterization

The compressional wave velocity (V_p) and shear wave velocity (V_s) are sensitive indicators of changes in pore structures and their fluid fills. V_p and V_s measurements provide critical information on the elastic properties of rocks, which are influenced by the type and distribution of fluids within the pore spaces. Variations in these velocities can reveal changes in porosity, pore connectivity, and fluid content, making them valuable for evaluating the effects of CO_2 injection. The compressional wave velocity (V_p) and shear wave velocity (V_s) in a rock are determined by its elastic properties and density. The fundamental equations for V_p and V_s are given by:

$$V_p = \sqrt{\frac{K + \frac{4}{3}\mu}{\rho}} \quad \text{and} \quad V_s = \sqrt{\frac{\mu}{\rho}} \quad (1)$$

Where V_p represents compressional wave velocity, V_s is shear wave velocity, K is the bulk modulus of the rock (a measure of the rock's resistance to uniform compression), μ is the shear modulus of the rock (a measure of the rock's resistance to shear deformation), and finally ρ represents the density of the rock. Based on the Equation given, any reduction in the stiffness or hardness of the rock, such as that caused by dissolution processes, will result in a lower compressional velocity. Conversely, precipitation processes that enhance the hardness and stiffness of the rock will lead to an increase in compressional velocity. These changes are crucial for understanding the effects of CO₂ injection on the mechanical properties of shale formations.

In this thesis study, by integrating dielectric permittivity, NMR, V_p , and V_s techniques, we investigate the impact of CO₂ treatment on shale samples through a systematic approach involving three stages which will be discussed in the methodology section. This methodology aims to reveal how CO₂ injection affects the pore structure and fluid distribution in shale, providing insights for effective CO₂ sequestration strategies.

2.4 CO₂ Sequestration in Unconventional Hydrocarbon Reservoirs

Shale formations are becoming a promising site for CO₂ geological sequestration due to their widespread occurrence and relatively large storage capacity potential. CO₂ sequestration within shale presents a rather complex, multi-scale process, encompassing spatial dimensions ranging from the nano to the kilometer scale (Wang et al., 2023). In organic-rich mature shale, the sequestered CO₂ will face a “competitive adsorption” with CH₄ residing in the shale. It is believed that a high injection rate will induce fractures, which can host the injected CO₂ along with the pre-existing fractures in the shale matrix. Absorption and desorption within the organic matter are formation pressure dependent (Wang et al., 2024; Lu et al., 2022).

Goodman et al. (2014) and Murugesu et al. (2023) indicated that there is a positive relationship between CO₂ adsorption capacity and TOC within shale formations, and the CO₂ to methane adsorption ratio is around 5:1 on kerogens. CO₂ adsorption capacity increases with shale thermal maturity as well. Their studies consider the storage of CO₂ both as a free phase within fractures and matrix pores and as a phase adsorbed into kerogen and clays. Moreover, the high adsorption capacity of the clay-rich shale is the reason why shale is considered a suitable host for CO₂.

Hazarika et al. (2023) stated that mineralogical composition, pore structure, and rock geomechanics are the main controls of the adsorption capacity. The ability of gas adsorption depends on swelling and retention capacity as well as the exchange of cations. One of (Goodman et al., 2014) proposed shale formations for CO₂ storage is the Eagle Ford shale formation, which will be utilized during this study. Finally, understanding the CO₂-fluid-rock interaction is critical to have a better evaluation of the seal integrity to avoid CO₂ leakage if it was injected in a saline aquifer with a nonpermeable shale seal above the targeted aquifer (Cheng et al. 2024).

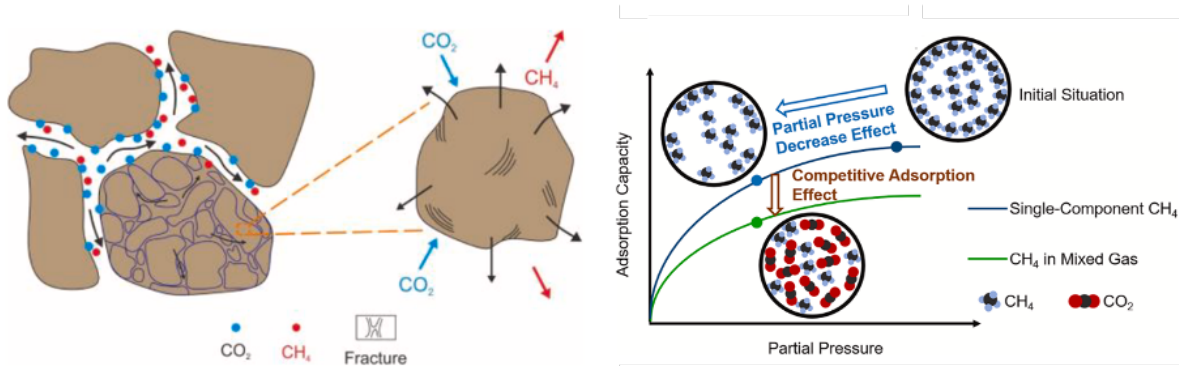


Figure 3. A competitive adsorption of CO₂-CH₄ and CH₄ desorption in shale (Wang et al., 2024 and Lu et al., 2022).

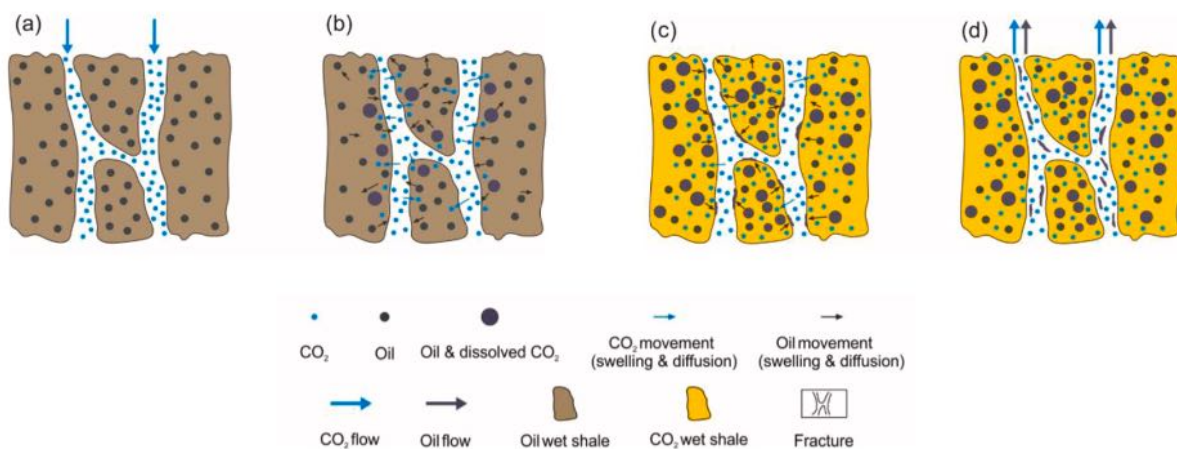


Figure 4. A schematic diagram showing from a to c; natural and newly formed fractures, CO₂ movement in organic matter, oil desorption and forming of CO₂ wet shale, and finally oil and CO₂ flowing in the fractures due to pressure reduction (from Wang et al., 2024)

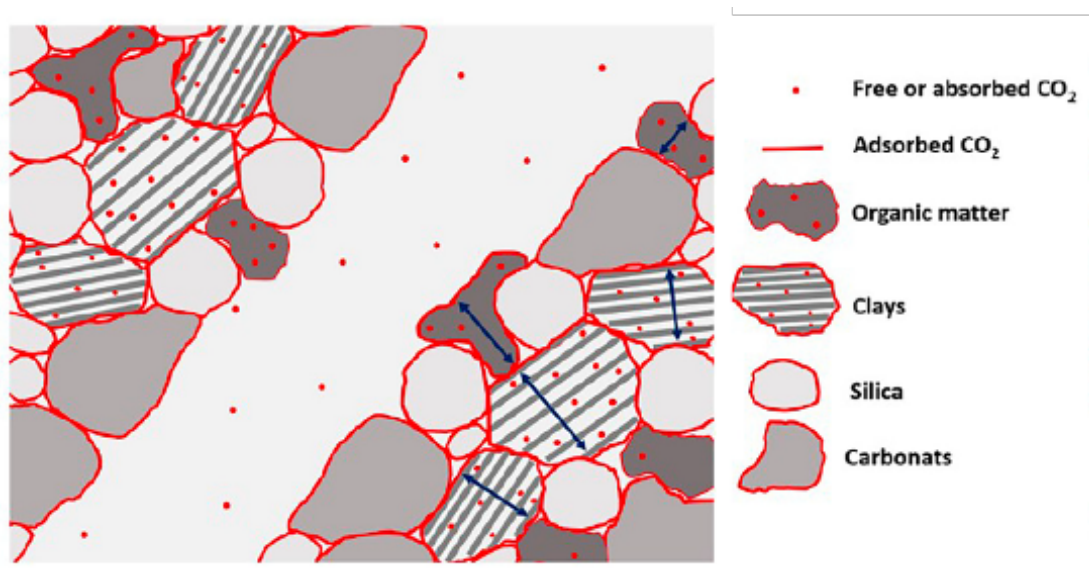


Figure 5. Different shale formation minerals reactions with CO₂ (Hazarika et al., 2023)

2.5 Isotope Geochemistry

2.5.1 Carbon, Oxygen and Sulfur

Carbon (6 Protons) exists naturally in three isotopes. ^{12}C and ^{13}C are stable isotopes with abundances of 98.90% and 1.10% respectively, and ^{14}C is the third radioactive isotope with a half-life of $\sim 5,730$ years (Faure & Mensing, 2005). Carbon stable isotopes are fractionated by chemical and biological processes in nature and can be found in the atmosphere, biogenic carbonates, and organic compounds.

As well as Carbon, Oxygen (8 protons) exists in nature in three stable isotopes. ^{16}O , ^{17}O and ^{18}O isotopes with abundances of 99.762%, 0.038% and 0.200% respectively (Faure & Mensing, 2005).

Finally, Sulfur (16 protons) exists naturally in four stable isotopes, ^{32}S , ^{33}S , ^{34}S and ^{36}S . The ratio of their abundances is from ^{32}S to ^{36}S 95%, 0.75%, 4.19% and 0.014% (Sharp, 2007).

The stable isotopes of elements fractionate when they transition between physical states or during chemical reactions within compounds. The degree of fractionation between two isotopes of the same element is mainly influenced by their differing masses and the temperature of the surroundings. The isotopic composition variations of these elements provide valuable insights into physical, geochemical, and geobiological processes that have affected the elements.

2.5.2 Stable Isotope Analysis

[Rosso, \(2013\)](#) discussed the importance of understanding the characteristics of supercritical CO₂, as it is essential for forecasting its subsurface behavior and monitoring sequestration systems and sites. The discussion extended to embracing the possibility of utilizing brine migration as a tracer for CO₂ migration from sequestered formations; injected CO₂ in brine will affect the isotope kinetics, hence the fractionation of carbon and oxygen might occur due to dissolution.

The isotopic composition variations of these elements provide valuable insights into the physical, geochemical, and geobiological processes that have affected the rock ([Faure & Mensing, 2005](#)). Several publications discussed CO₂–water–rock interactions ([Myrntinen et al., 2010, 2012](#); [Humez et al., 2014](#); [Serno et al., 2017](#)), and concluded that dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) values can be considered as a reliable trace to monitor the injected CO₂ in aquifers. As well as that, multi-isotopic approaches to geochemical processes are applicable for monitoring and alarming CO₂ leakage. [Myrntinen et al. \(2010\)](#) discussed the first study of on-shore CO₂ injection in Europe, at the Ketzin site which started in June 2008. The concept discussed in the paper was about CO₂ geochemical trapping through solubility and ionic trapping within the fluids in the subsurface. Geochemical trapping is affected by several factors, such as salinity, PH, pressure, temperature, and finally microbial activities. The $\delta^{13}\text{C}_{\text{CO}_2}$ of the injected CO₂ is mainly originated from C₃ plant material with values ranging from -23 to -33 ‰, and the $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in the aquifer is around -10 ‰. The results of $\delta^{13}\text{C}_{\text{DIC}}$ values after injection reported a negative shift for all three wells. On the other hand, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ didn't record a significant change and remained at around -5.5‰. The 9-month monitoring study concluded that $\delta^{13}\text{C}_{\text{DIC}}$ values can be considered as a reliable trace to monitor the injected CO₂ in aquifers.

A follow-up laboratory study by [Myrtingen et al. \(2012\)](#) further examined water–rock–CO₂ dynamics. As in a previous publication by the same author, geochemical trapping in the experiment is limited to DIC solubility and ionic trapping, mineral trapping is exempt from the experiment. Three experiments were performed on quartzitic limestone from the Aquitaine basin that consists of 70% calcite, 27% quartz, and 3% clay minerals and goethite. The results were delivered in three phases: baseline, pre-CO₂ breakthrough, and finally post-CO₂ breakthrough. The recorded difference value was around 18.4‰, which coincides with the values reported from the Ketzin site.

The conclusion of the study again embraces that $\delta^{13}\text{C}_{\text{DIC}}$ is a reliable tracer of the injected CO₂ with different behaviors during each phase. [Humez et al. \(2014\)](#), shared another interesting result of the 2011 shallow subsurface CO₂ injection trial, which took place at the CO₂FieldLab close to Svelvik, Norway. Water samples of varying depths (5 to 15m) were collected at different phases of the CO₂ injection, starting from the initial baseline conditions to post-injection. The analyses include measurements of groundwater PH, temperature, and electrical conductivity, as well as isotope analysis. The main discussion in the paper was about differentiating between reactive mechanisms, non-reactive processes (such as mixing), and CO₂–water-rock interactions linked to CO₂ leaks, which are promising for investigating CO₂ leakage on a larger scale. The variation in $\delta^{13}\text{C}_{\text{DIC}}$ differed at each depth, displaying the complex behavior of CO₂ mixing due to its different sources (including atmospheric, biogenic, and injected). Nevertheless, due to the limited presence of carbonates in the aquifer and the diversity of carbon sources, $\delta^{13}\text{C}$ alone was not effective in this water-rock interaction tracking experiment. Different isotope systems such as $[\delta^2\text{H}-\delta^{18}\text{O}]_{\text{H}_2\text{O}}$ and $[\delta^{34}\text{S}-\delta^{18}\text{O}]_{\text{SO}_4}$ clarified some mixing processes and CO₂ movement, as well as strontium, boron, and lithium isotopes analyses. This study concludes that multi-isotopic approaches to geochemical processes are applicable for monitoring and alarming CO₂ leakage, yet their implementation could be costly.

[Serno et al. \(2017\)](#) reviewed field and laboratory experiments measuring oxygen isotopes in both the injected CO₂ and produced water to estimate the residual and structural trapping mechanisms of the stored CO₂. Prior to the injection of CO₂, the oxygen isotope of water and the injected CO₂ can reach equilibrium in a matter of days. Another oxygen value shift is expected due to the mineral alteration process in the reservoir water, which releases oxygen previously incorporated into mineral structures, particularly carbonate. However, the impact of this mechanism on alterations in the $\delta^{18}\text{O}$ values of reservoir water is typically minor compared with the response to the injected CO₂.

[CHAPTER 3

GEOLOGICAL SETTINGS]

Two different carbonate mudrocks (shales) will be examined in this study. The first one is from the Upper Cretaceous Muwaqqar Chalk Marl Formation (MCM) in Jordan, which was deposited under anoxic marine conditions with high TOC and sulfur content. These rocks are of kerogen-type IIS with mainly alginate and amorphous organic matter and planktonic foraminifera assemblages ([Abu-Mahfouz et al. 2019](#); [Hakimi et al., 2016](#)). The second one is from the Upper Cretaceous Eagle Ford formation from the USA, which was mainly deposited in a flooded marine continental shelf environment and contains type II and III kerogens with around 3.2 wt% TOC ([Hou et al., 2021](#)). Both the southern parts of the USA and Jordan were situated at a latitude of approximately 20 to 30 degrees north of the equator during the Cretaceous period. This positioning placed them in a tropical to subtropical climate, much warmer and more humid than their current climate. Overall, The Cretaceous period marks a relatively warm period in the Earth's history with higher sea levels. Nevertheless, it is noticed that paleowater conditions had different sedimentation control on the shales, which could be because of the tectonism that created graben basins ([Hakimi et al., 2018](#)). Graben basin inversion in the Syrian arc and extensional tectonism in northern Jordan took place during the Late Cretaceous through the Paleogene, causing the formation of the Azraq-Sirhan Rift Graben ([Lüning & Kuss, 2014](#)).

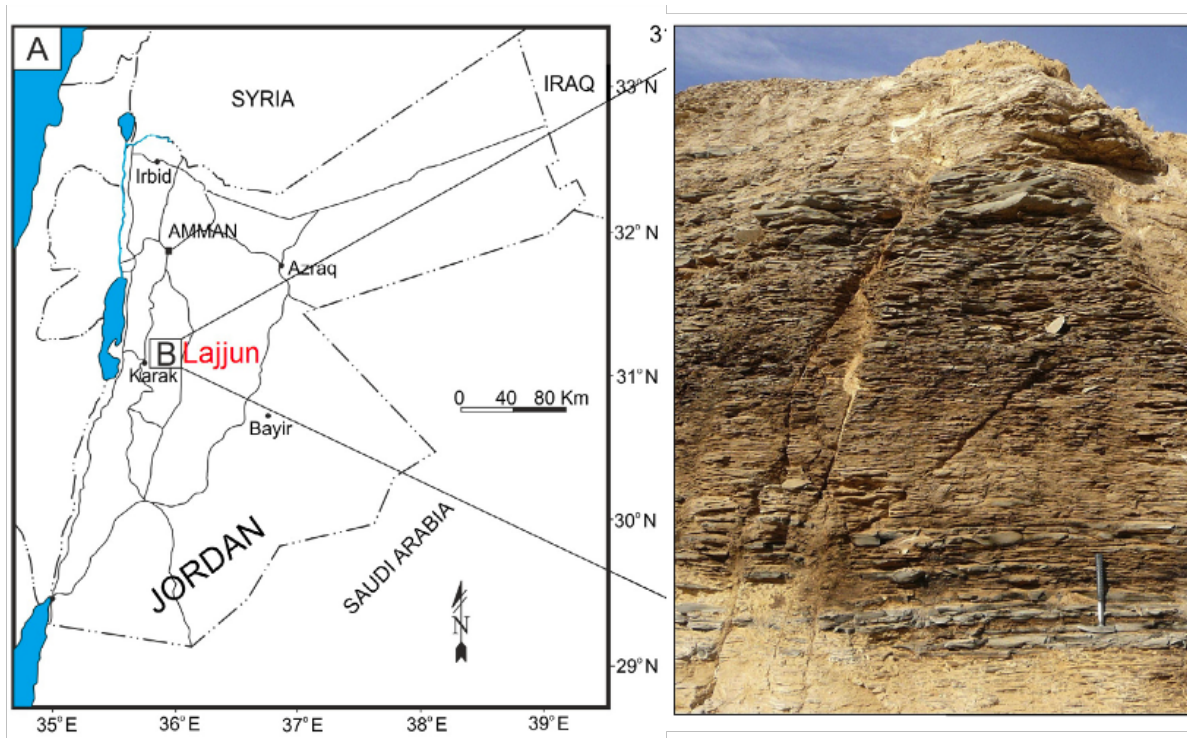


Figure 6. Central and southern Jordan stratigraphic column of the Upper Cretaceous strata (Abu-Mahfouz et al., 2022)

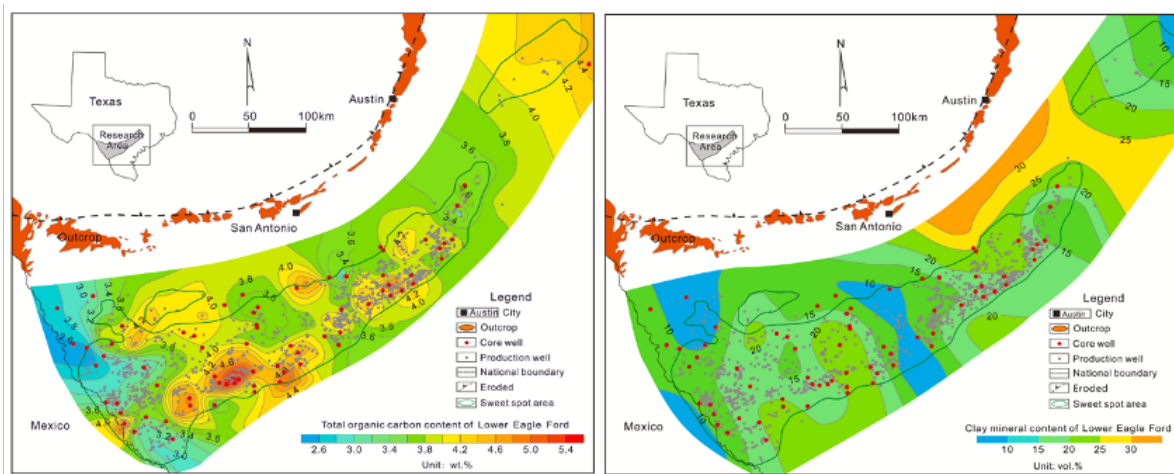


Figure 7. Contoured maps showing TOC wt. % and clay content of Lower Eagle Ford shale (Hou et al., 2021)

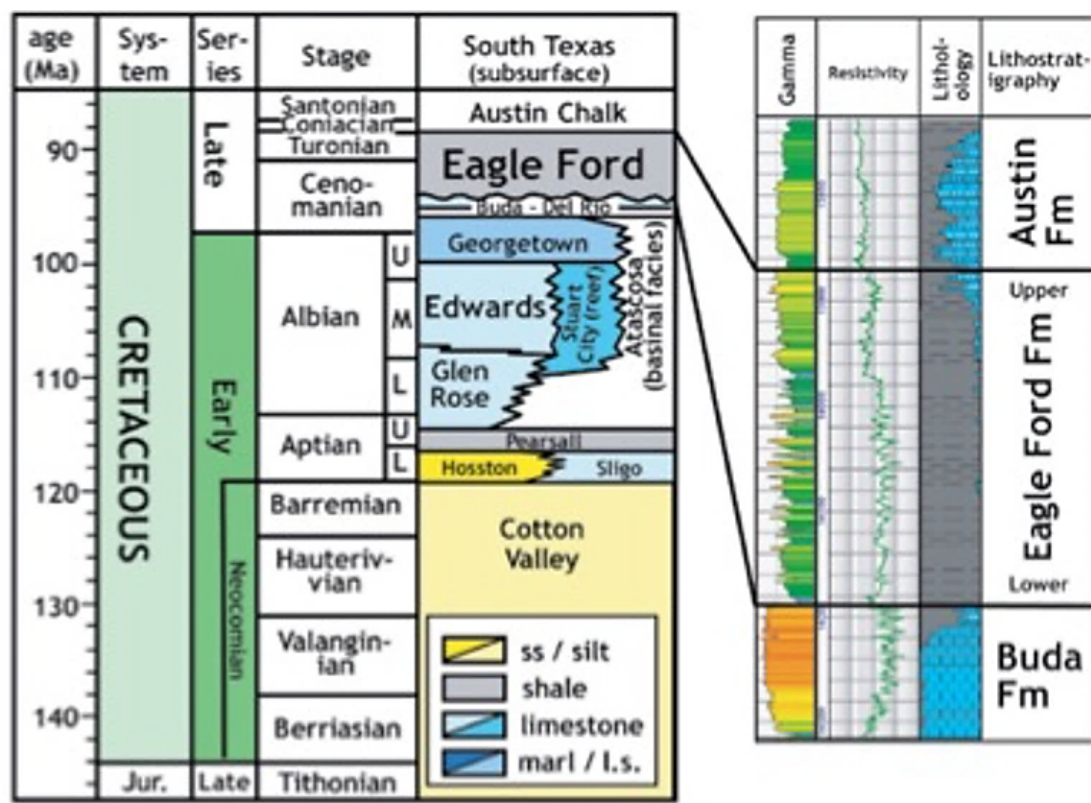


Figure 8. Eagle Ford stratigraphic column along with well log for the same interval (Ratcliffe et al., 2012)

[CHAPTER 4

METHODOLOGY]

4.1 Sample Selection and Preparation

The two shale samples were divided into two main types: core and powdered samples. The core samples were taken for petrophysical analysis, with precise dimensions of approximately 53 mm in length and 37.26 mm in diameter, these samples were analyzed after each treatment stage starting from initial dry analysis, brine-saturated, and CO₂-treated. For the powdered samples for geochemical and isotopic analyses, the treatment stages were dry, dry CO₂-treated, and liquid brine CO₂-treated. Since the Shale samples in the study are immature, further artificial maturation on the samples was performed at 250 °C for two days with an aim to have them around the late oil to condensate stage to investigate the effect of maturity on the CO₂ treatment. The same treatment stages of the immature samples were conducted on the matured samples (dry CO₂-treated, and liquid brine CO₂-treated).

4.2 CO₂ Treatment Workflows

4.2.1 Powdered Sample CO₂ Treatment Workflow

The powdered samples were divided into two types: dry and wet/ immersed in 3% KCl liquid brine. Both types of samples were treated with CO₂ for one week individually. Throughout the entire experiment period, the samples were maintained under a confined pressure of 1,300 psi and at a temperature of approximately 45 degrees Celsius. CO₂ was injected and lifted along with all samples to simulate CO₂ sequestration conditions.

4.2.2 Core Sample CO₂ Treatment Workflow

The core plug samples were saturated in liquid brine for two days to ensure that the samples were brine-saturated prior to treatment with CO₂. The saturated samples were then treated with CO₂ for 30 days. Throughout the entire experiment period, the samples were maintained under a confined pressure of 1,300 psi and at a temperature of approximately 45 degrees Celsius. Keeping the samples under such conditions was proposed to simulate the dynamic process of subsurface CO₂ sequestration. This approach aimed to capture variations in the petrophysical and geo-mechanical characteristics of the tested shale samples. After completing the treatment, workflow, and all analyses, the samples were washed for two days to clean them from salts produced by the CO₂ treatment and then they were saturated again in liquid brine for two days as preparation for a computerized tomography (CT) scan and NMR analysis.

4.3 Analytical Techniques

4.3.1 Geochemical Analysis

Samples are powdered and then split into several portions as they were carried out for different labs for different analyses. The first analysis done was in the inorganic lab, which is X-ray diffraction analysis (XRD) and X-ray fluorescence analysis (XRF) to characterize the mineralogical and elemental composition of the samples before and after CO₂ treatment. XRD and XRF analyses help in understanding the abundance of minerals within the samples which eventually indicates the rock type, depositional environment as well as chemical reactions within the sample due to the CO₂ treatment. Around 50mg of each powdered sample was used for pyrolysis analysis on Rock-Eval (7S) to acquire S1, S2 (and Tmax), S3, TOC (%), and Total S content (%). Pyrolysis analysis in this study helped in quantifying the organic content in the samples as well as understanding the thermal maturity and quality of the kerogen within the rock samples. The results of this analysis are reported in wt.% for TOC and TS, mg/g rock for S1 and S2, and finally, °C for Tmax calculated on the S2 peak.

The last portion of the powdered sample was taken to conduct Carbon, Oxygen, and Sulfur isotopic analyses by gas chromatography isotope ratio mass spectrometry instrument (GC-IRMS). Multiple calibration standards and sample duplicates were run before and after samples. Samples' results of isotope values are reported as per mil difference from their standards: Vienna PeeDee Belemnite (VPDB) for carbon and oxygen, and finally Vienna Canyon Diablo Troilite (VCDT) for sulfur.

4.3.2 Petrophysical Analysis

The analyses on the core samples were conducted in three stages to evaluate the impact of CO₂ treatment on the pore structure and fluid distribution within the shale samples. The dry samples' initial analysis established a detailed baseline for pore structure, dielectric properties, and elastic properties VP/VS. This was followed by brine saturation to observe the effects of brine saturation on the same parameters. The brine saturation of the dry samples was conducted by submerging the samples in pressurized brine water for 48 hours to ensure full saturation. Finally, for the CO₂-treated samples, the analyses helped in assessing the impact of CO₂ treatment on the pore structure, fluid distribution, and dielectric properties of the two different shale core samples. The analyses conducted on the samples are dielectric permittivity, conductivity, NMR, Vp, and Vs measurements. The permittivity and conductivity values were recorded and analyzed to determine changes in pore structure and fluid distribution, while in NMR, the relaxation times were interpreted to determine the pore size distribution and the mobility of fluids within the pores. Measurements of Vp and Vs were conducted on the samples at each stage to evaluate the effects of fluid saturation and CO₂ treatment on the rock's mechanical properties. Changes in these velocities were analyzed to interpret alterations in porosity, pore connectivity, and fluid content. CT scan analysis was conducted on non-treated sister samples and on the cleaned and saturated core samples to see the internal structure effect induced by the treatment.

4.3.3 Microscopic Imaging

Throughout all stages of the CO₂ treatment including the maturation stages, shale chip samples were assured to be collected and kept for Scanning Electron Microscopy (SEM) analysis. The microscopic analysis is meant to be a complementing analysis demonstrating the CO₂ effect in the shale rocks in terms of porosity, microstructures, mineral composition, and distribution, as the samples were for all stages of the CO₂ treatment.

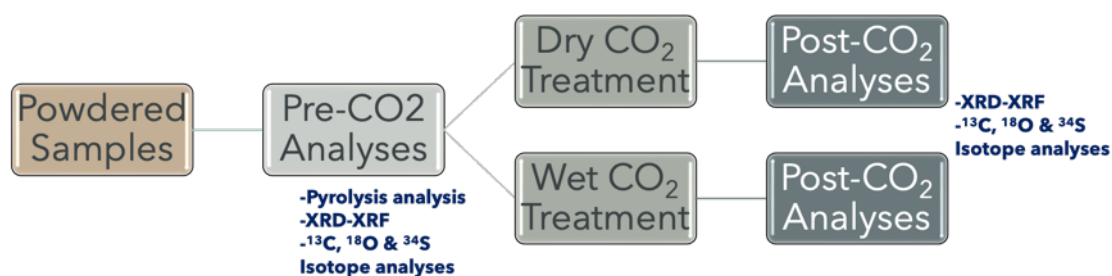


Figure 9. The workflow followed for the analysis of the powdered samples

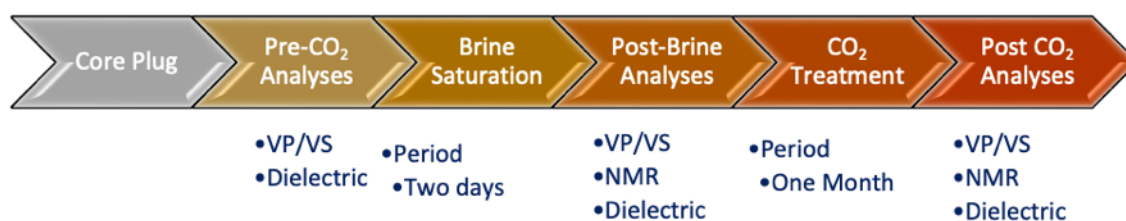


Figure 10. The workflow followed for the analysis of the core plugs



Figure 11. CO₂ Treatment Conditions for both the powdered and core sample

[CHAPTER 5

RESULTS]

The results will be reported in three main sections: geochemical analysis results for the powdered samples, petrophysical analysis results for the core samples, and SEM images of the surface morphology of the sample chips.

Isotopic geochemical analysis results are reported here following the same CO₂ treatment phases; results from initial analysis, results from liquid brine CO₂ treated samples, and results from dry CO₂ treated samples. In addition, results obtained from the artificially matured stage of the carbonate mudrocks are also reported. The petrophysical results are also reported for the three phases: dry sample results (the values of the sample without brine saturation or CO₂ treatment), followed by results from brine-saturated samples, and finally from CO₂_treated samples.

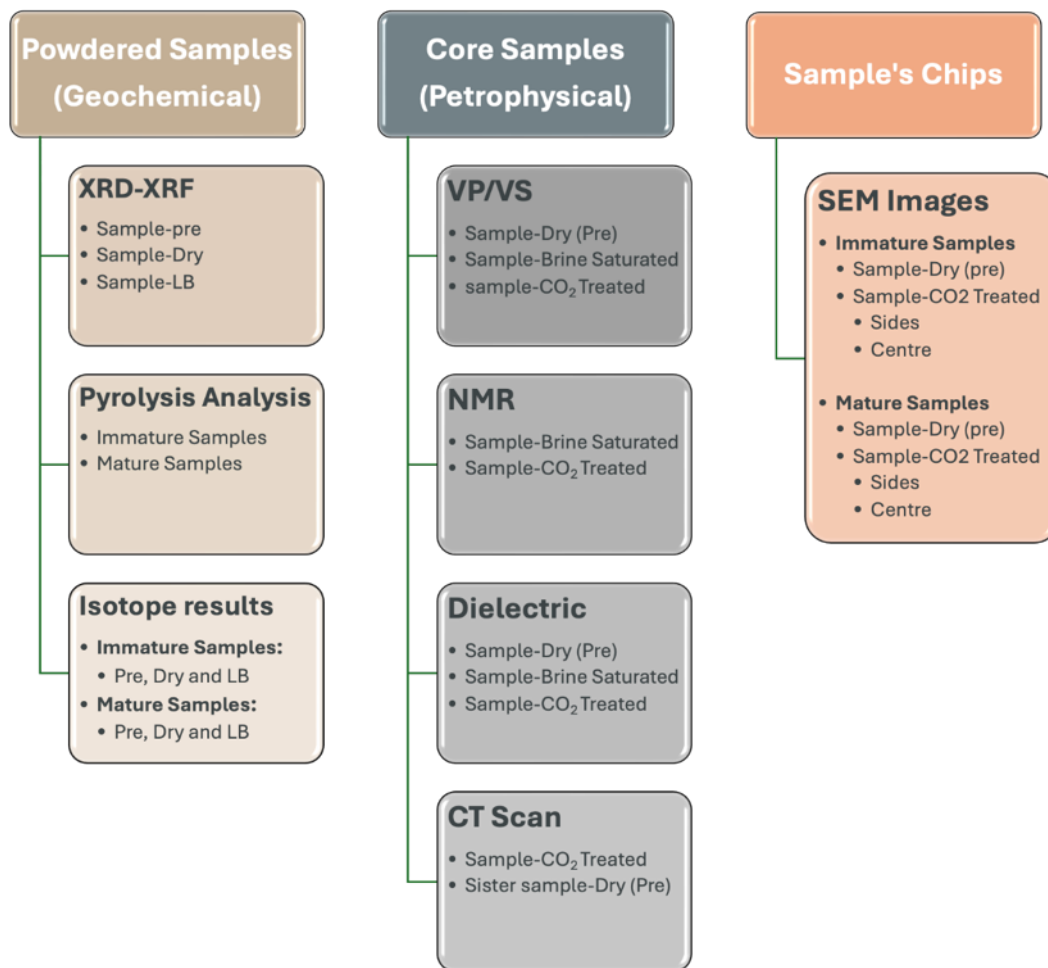


Figure 12. Overview of types of samples and analysis results data

5.1 Geochemical analysis

5.1.1 Mineralogical Composition

XRD results of the samples pre-CO₂ treatment showed that the most dominant mineral in both samples is calcite with 53% in Jordanian Shale (JS) and 84% in Eagle Ford (EF), followed by only quartz in EF with 16%. In contrast, the JS sample contained 29% of kaolinite, followed by 12% quartz and around 6% of pyrite and gypsum. Moreover, Post-CO₂ Treatment XRD results showed that calcite is still the most dominant in all samples yet with variation of liquid brine samples (-LB) and dry samples (-dry). JS-dry had around 52% calcite were JS-LB showed a calcite reduction to 23% of the sample weight. EF-dry and EF-LB calcite readings were 84% and 73%, respectively. Kaolinite presence in JS-dry and JS-LB ranged between 34 to 41%. Quartz readings were 11%, 18%, 12%, and 19% for JS-dry, JS-LB, EF-dry, and EF-LB respectively. Liquid brine samples of JS and EF contained sylvite with 14% for JS-LB and 4% for EF-LB.

Table 1. Mineralogical data for pre- and post-CO₂ treatment Powdered Samples

Sample ID	Calcite	Quartz	Kaolinite	Pyrite	Gypsum	Sylvite
JS-Pre	53.2	11.7	29.2	3.2	2.7	0
JS-Dry	51.5	11.3	33.8	3.4	0	0
JS-LB	22.5	18	40.8	4.4	0	14.3
EF-Pre	83.8	16.2	0	0	0	0
EF-Dry	83.6	12.1	3.8	0.5	0	0
EF-LB	72.7	18.6	4.4	0.5	0	3.7

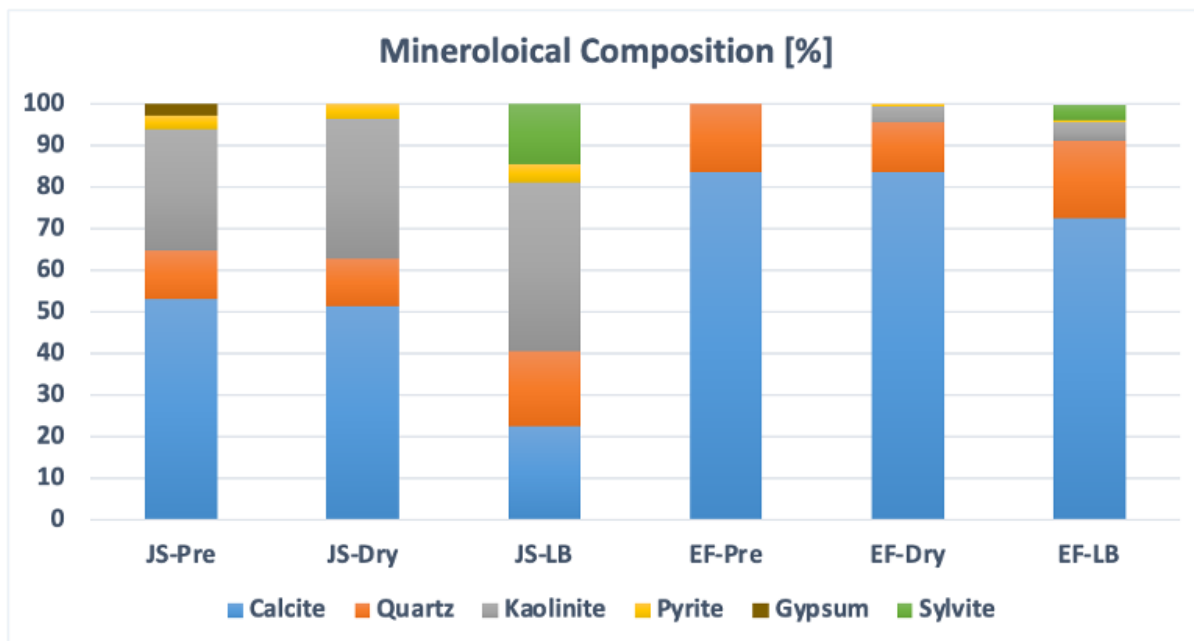


Figure 13. Mineralogical Composition plot for pre- and post-CO₂ treatment powdered Samples.

5.1.2 Elemental Composition

Pre-CO₂ treatment XRF results revealed that 65% of the JS sample is dominated by calcium and silicon elements, with the presence of aluminum, sulfur, and iron at around 30% of its weight. Elements potassium, phosphate, magnesium, and strontium form around 5% of the JS sample. Moving on to the EF sample, calcium and silicon are the most abundant elements with about 95% of the sample. Around 4% of the sample contained aluminum, sulfur, and iron, with only 1% of the sample weight for several elements which are potassium, magnesium, and strontium. Moving on to the post-CO₂ treatment XRD results, the data revealed that JS-dry still contains almost 65% of its weight calcium and silicon elements, with the presence of aluminum, sulfur, and iron with around 30% of its weight. However, the JS-LB sample contains only 39% of calcium and silicon. Moreover, around 59% of the sample was split between aluminum, sulfur, potassium, chlorine, and iron.

For EF samples, EF-dry contained roughly the same as EF-Pretreatment concentration percentages (calcium and silicon elements with cumulative concentration of 93%, and 4% of aluminum, sulfur and iron). EF-LB sample's calcium and silicon elements percentage reduced slightly to 83% (10% reduction), with around 14% of the sample were split between aluminum, sulfur, potassium, chlorine, and iron.

Table 2. Elemental data for pre- and post-CO₂ treatment Powdered Samples

Sample	JS-Pre	JS-Dry	JS-LB	EF-Pre	EF-Dry	EF-LB
Ca	39.59	41.59	16.51	82.02	80.93	63.22
Si	24.49	23.41	22.37	13.14	12.78	20.64
Al	10.40	9.94	9.48	1.55	1.49	2.37
S	10.82	10.08	12.00	1.15	1.16	1.62
Fe	9.90	10.20	11.65	0.94	1.85	5.08
K	2.14	2.13	15.18	0.28	0.28	3.45
Cl	0.00	0.00	10.33	0.00	0.01	2.33
P	1.16	0.95	1.09	0.00	0.02	0.00
Mg	0.61	0.58	0.34	0.28	0.52	0.53
V	0.19	0.19	0.19	0.07	0.08	0.08
Cr	0.16	0.18	0.29	0.00	0.21	0.14
Mn	0.01	0.02	0.02	0.07	0.08	0.08
Ni	0.03	0.08	0.17	0.00	0.10	0.09
Zn	0.09	0.12	0.17	0.02	0.02	0.02
Sr	0.40	0.50	0.20	0.46	0.47	0.35

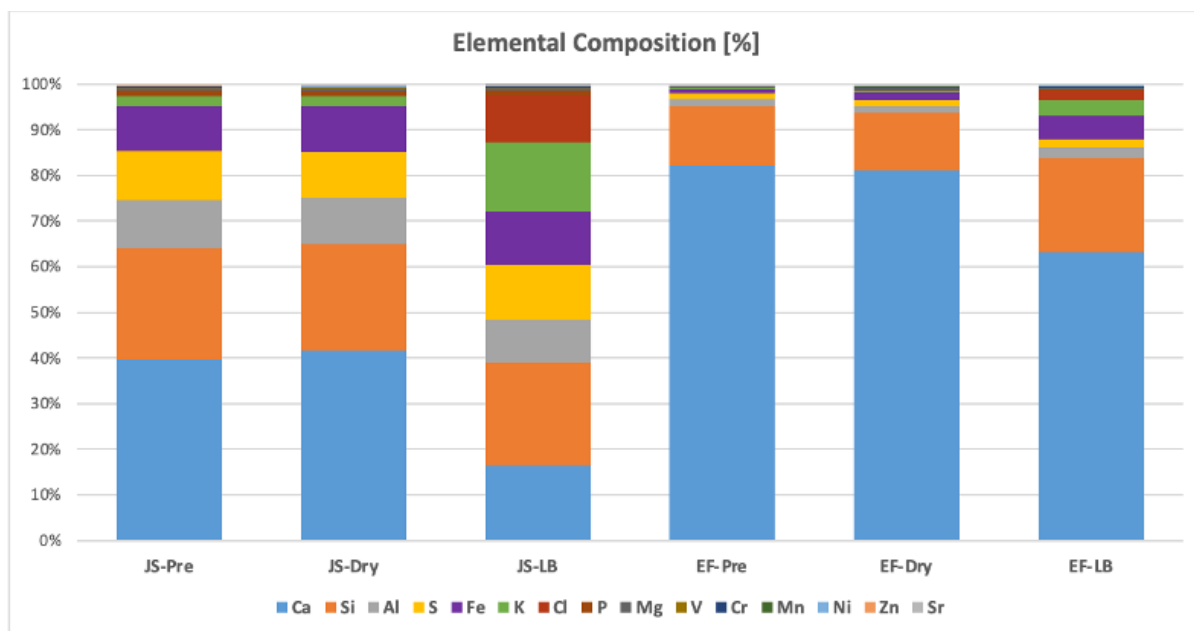


Figure 14. Elemental Composition plot for pre- and post-CO₂ treatment powdered samples

5.1.3 Pyrolysis Analysis

JS Immature sample from the bulk rock method showed a relatively low value of S1 (the amount of free HC) as it was around 4.4 mg/g of rock. However, the S2 (HC generated through thermal cracking of non-volatile organic matter) value was substantially high; 98.8 mg/g of rock. Tmax calculated on top of the S2 peak (the temperature at which release of HC from cracking of kerogen) was 416 °C with total organic carbon (TOC) of 12.22 wt. %, and around 3% of total sulfur. Hydrogen and oxygen index readings were 808 and 7, respectively. In comparison, the EF Immature sample showed low values of both S1 and S2; around 2 and 17 mg/g of rock respectively. As well as that, TOC was around 1.9 wt. % and TS was 0.5 wt. %.

Table 3. Pyrolysis Data for Immature and Mature Samples

Sample	S1 (mg/g)	S2 (mg/g)	Tmax (°C)	HI	TOC (%)	Total S (%)
JS_Immature	4.38	98.81	416	808	12.22	3.25
EF_Immature	1.9	16.95	432	578	2.9	0.49

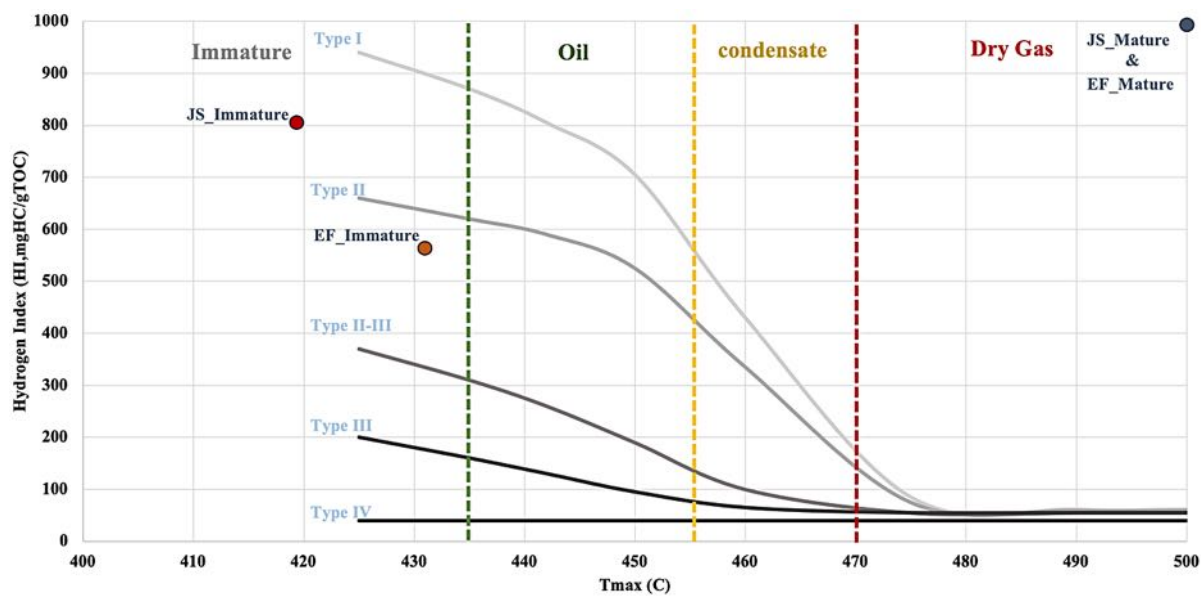


Figure 15. Pyrolysis plot for Immature and Mature samples, Mature Samples exceed the plot limits

5.1.4 Isotope Analysis

Starting with the immature Pre-CO₂ Treatment analysis, the JS sample showed a $\delta^{34}\text{S}$ value of -5.67 (‰ VCDT), which is heavier than the EF sample $\delta^{34}\text{S}$ value of -18.53‰. EF sulfur Isotope analysis barely produced a peak at all, thus more sample weight had to be added to produce a reading of $\delta^{34}\text{S}$. $\delta^{13}\text{C}$ (‰VPDB) and $\delta^{18}\text{O}$ (‰VPDB) values of JS are -1.59 ‰ and -2.26 ‰ respectively. EF Isotope readings were -0.78 ‰ for $\delta^{13}\text{C}$ and -6.99 ‰ for $\delta^{18}\text{O}$.

After CO₂ Treatment of the immature samples, JS samples showed $\delta^{34}\text{S}$ values of -7.54‰ for JS-dry and -9.15‰ for JS-LB. $\delta^{13}\text{C}$ values of JS are -1.63 ‰ and -4.00 ‰ for JS-dry and JS-LB respectively. Finally, for the JS sample, the value of $\delta^{18}\text{O}$ for JS-dry was -1.73‰, and for JS-LB the value was -2.92‰. EF-Dry Isotopes readings were as follows: -16.87 ‰ for $\delta^{34}\text{S}$, and -1.33 ‰ $\delta^{13}\text{C}$ and -7.36 ‰ for $\delta^{18}\text{O}$. Finally, EF-LB isotopes were -12.06 ‰ for $\delta^{34}\text{S}$, and -2.25 ‰ $\delta^{13}\text{C}$ and -6.99 ‰ for $\delta^{18}\text{O}$.

Isotopic analyses were conducted on the same stages for the artificially matured samples, and the results of the mature Pre-CO₂ Treatment samples showed that $\delta^{13}\text{C}$ (‰VPDB) and $\delta^{18}\text{O}$ (‰VPDB) for JS are -1.36 ‰ and -1.93 ‰ and for EF are -0.76 ‰ and -7.01 ‰ respectively.

When those samples were treated with CO₂, JS sample $\delta^{13}\text{C}$ values were -1.60 ‰ and -1.53 ‰ for JS-dry and JS-LB, and $\delta^{18}\text{O}$ values were -1.69 ‰ for JS-dry and -1.77 ‰ for JS-wet. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of EF-Dry sample are -0.85 ‰ and -6.96 ‰, and finally EF-LB values are -0.87 ‰ for $\delta^{13}\text{C}$ and -7.17 ‰ for $\delta^{18}\text{O}$.

Table 4. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ isotope data for all stages of the immature and mature samples

Sample ID	$\delta^{13}\text{C}$ (‰VPDB)	$\delta^{18}\text{O}$ (‰VPDB)	$\delta^{34}\text{S}$ (‰ VCDT)
Immature_JS-Pre	-1.59	-2.26	-5.67
Immature_JS-dry	-1.63	-1.73	-7.54
Immature_JS-LB	-4.00	-2.92	-9.15
Mature_JS-Pre	-1.36	-1.93	NA
Mature_JS-dry	-1.60	-1.69	6.95
Mature_JS-LB	-1.53	-1.77	4.61
Immature_EF-Pre	-0.78	-6.99	-18.53
Immature_EF-dry	-1.33	-7.36	-16.87
Immature_EF-LB	-2.25	-6.99	-12.06
Mature_EF-Pre	-0.76	-7.01	-13.60
Mature_EF-dry	-0.85	-6.96	8.57
Mature_EF-LB	-0.87	-7.17	2.46

5.2 Petrophysical Analysis

5.2.1 VP/VS Results

Starting with the JS sample, JS_dry VP and VS values were 2231 M/S and 1360 M/S, respectively. JS_brine_saturated values were 2543 M/S for VP and 2329 for VS, while JS_CO₂_Treated VP value was 1420 M/S with no VS value as it was analyzed by the ProCeq instrument. VP/VS analysis was repeated after cleaning the CO₂-treated samples from salts and saturating them with brine for two days. The JS_post_cleaning VP value was 2643 M/S and with no VS value as there were no wave to pick. The Vp/Vs ratio of the JS_pre-treated sample is 1.64.

For EF sample, the VP values were 5445 M/S Dry, 5533 M/S Brine_Saturated, 5230 M/S CO₂_Treated, and finally, 5459 M/S for the post_cleaning sample. EF VS values are 2932 M/S Dry, 2570 M/S Brine Saturated, 2100 M/S CO₂_Treated, and 3138 M/S for Post Cleaning. The Vp/Vs ratios of the EF sample are 1.86 for the pre-treated sample and 1.74 for the post-cleaning sample.

Table 5. Vp/Vs Values of JS and EF samples for all stages

Sample	Vp (M/S)	Vs1 (M/S)	Vs2 (M/S)	Vp/Vs Ration
JS-Dry (PRE)	2231	1360	1361	1.64
JS-Bine_Saturated	2543	2345	2329	1.09
JS-CO ₂ _Treated	1420			
JS-Post_Cleaning	2643			
EF-Dry (PRE)	5445	2909	2932	1.86
EF-Bine_Saturated	5533	2721	2570	2.15
EF-CO ₂ _Treated	5230	2103	2100	2.49
EF-Post_Cleaning	5459	3138	3146	1.74

5.2.2 NMR Results

Initially, JS and EF samples were examined by NMR after brine saturation and CO₂ treatment. For JS Brine_Saturated the dominant T2 peak was observed at 2.818 with 1.966 T2 log mean. After CO₂ treatment, JS CO₂_Treated sample dominant T2 peak was observed at 3.162 with 2.292 T2 log mean. Total porosities for JS were 16.3 p.u for the brine_saturated, and 17.3 p.u for CO₂_Treated. For the EF sample, dominant T2 peaks were observed at 0.316 with 0.504 T2 log mean for Brine_Saturated and 0.398 with 1.024 T2 log mean for CO₂_Treated. The total porosities for EF were 0.55 p.u for the brine_saturated sample and 0.776 p.u for CO₂_Treated. Further stages were done after the CO₂ treatment of the samples, which was cleaning both cores from salts and then brine saturating them to investigate the porosity reading of the EF sample specifically. After Cleaning the samples, the JS sample dominant T2 peak was observed at 3.162 with 2.756 T2 log mean, and the second peak was at 0.125 p.u. EF sample dominant T2 peaks were observed at 0.282 with a 2.361 T2 log mean. The total porosities for the samples were 21.0 p.u for the JS sample, and 0.913 p.u for the EF sample. The two stages of plots shown in Figures 16 and 17 represent 1) the brine-saturated stage (blue) and 2) the final stage after CO₂ treatment, cleaning from salts and brine saturation (red).

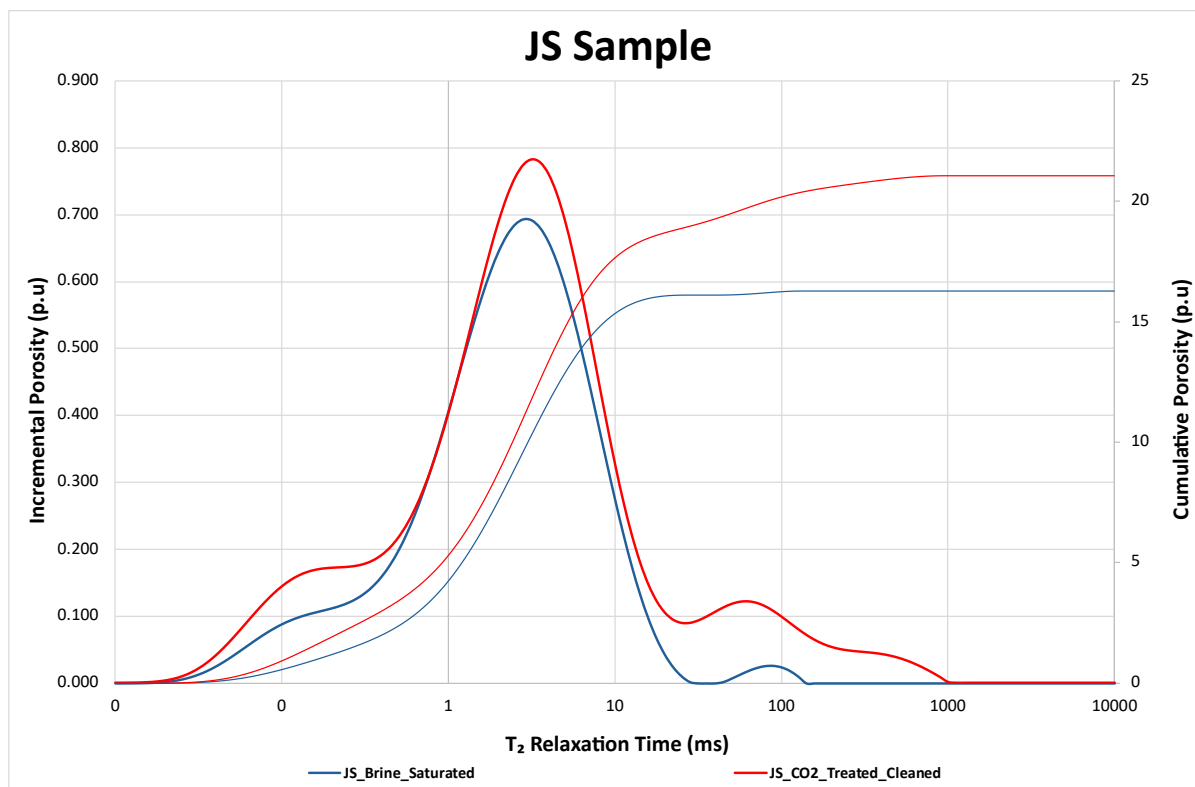


Figure 16. NMR results for all stages of the JS sample

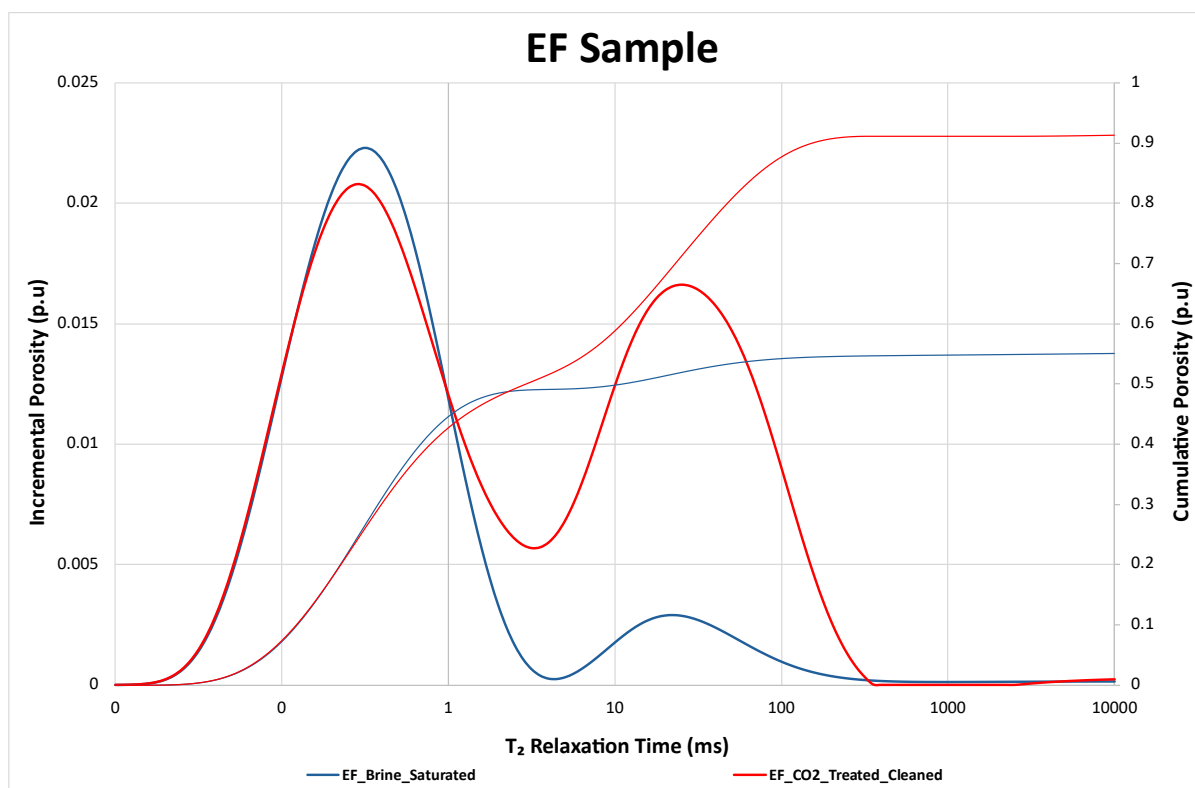


Figure 17. NMR results for all stages of EF sample

a) JS Gravitational Porosity Calculation

Volume of the Core Plug Calculation:

The formula for the volume V of a cylinder is:

$$V = \pi r^2 h \quad (2)$$

where:

- r is the radius of the cylinder,
- h is the height (or length) of the cylinder.

Given:

- Diameter $d = 37.26$ mm, so the radius $r = d/2 = 37.26/2 = 18.63$ mm.
- Length $h = 52$ mm.

Volume Calculation:

$$V = \pi(18.63)^2(52)$$

$$V \approx 3.14159 \times 347.0769 \times 52$$

$$V \approx 3.14159 \times 18048.00$$

$$V \approx 56715.17 \text{ mm}^3$$

Cubic millimeters to cubic centimeters ($1 \text{ cm}^3 = 1000 \text{ mm}^3$):

$$V \approx 56715.17 \text{ mm}^3 \times 1 \text{ cm}^3 / 1000 \text{ mm}^3 = 56.72 \text{ cm}^3$$

Volume of the Pore Space Calculation:

The volume of the pore space is calculated from the difference in the wet and dry weights of the core plug, assuming the density of the brine.

Given:

- Dry weight $W_d = 103$ g,
- Wet weight $W_w = 111.27$ g,
- Density of brine $\rho_{\text{brine}} = 1.01 \text{ g/cm}^3$.

The weight of the brine in the pore space is:

$$W_{\text{brine}} = W_w - W_d = 111.27\text{g} - 103\text{g} = 8.27\text{g}$$

The volume of the pore space V_{pores} can be calculated using the density of the brine:

$$V_{\text{pores}} = W_{\text{brine}} / \rho_{\text{brine}} = 8.27\text{ g} / 1.01\text{ g/cm}^3 \approx 8.19\text{ cm}^3$$

Porosity Calculation:

Porosity ϕ is defined as the ratio of the volume of the pore space to the total volume:

$$\phi = V_{\text{pores}} / V_{\text{pores}} = 8.19\text{ cm}^3 / 56.72\text{ cm}^3 \approx 0.1444$$

Percentage Conversion:

$$\phi \approx 0.1444 \times 100\% \approx \mathbf{14.44\%}$$

b) EF Gravitational Porosity Calculation

Volume of the Core Plug Calculation:

The formula for the volume V of a cylinder is:

$$V = \pi r^2 h \quad (2)$$

where:

- r is the radius of the cylinder,
- h is the height (or length) of the cylinder.

Given:

- Diameter $d = 37.26$ mm, so the radius $r = d/2 = 37.26/2 = 18.63$ mm.
- Length $h = 53$ mm.

Volume Calculation:

$$V = \pi(18.63)^2(53)$$

$$V \approx 3.14159 \times 347.0769 \times 53$$

$$V \approx 3.14159 \times 18395.0767$$

$$V \approx 57782.96 \text{ mm}^3$$

Cubic millimeters to cubic centimeters ($1 \text{ cm}^3 = 1000 \text{ mm}^3$):

$$V \approx 57782.96 \text{ mm}^3 \times 1 \text{ cm}^3 / 1000 \text{ mm}^3 = 57.78 \text{ cm}^3$$

Volume of the Pore Space Calculation:

The volume of the pore space is calculated from the difference in the wet and dry weights of the core plug, assuming the density of the brine.

Given:

- Dry weight $W_d = 153.24$ g,
- Wet weight $W_w = 153.56$ g,
- Density of brine $\rho_{\text{brine}} = 1.01 \text{ g/cm}^3$.

The weight of the brine in the pore space is:

$$W_{\text{brine}} = W_w - W_d = 153.56 \text{ g} - 153.24 \text{ g} = 0.32 \text{ g}$$

The volume of the pore space V_{pores} can be calculated using the density of the brine:

$$V_{\text{pores}} = W_{\text{brine}} / \rho_{\text{brine}} = 0.32 \text{ g} / 1.01 \text{ g/cm}^3 \approx 0.3178 \text{ cm}^3$$

Porosity Calculation:

Porosity φ is defined as the ratio of the volume of the pore space to the total volume:

$$\varphi = V_{\text{pores}} / V_{\text{total}} = 0.3178 \text{ cm}^3 / 57.78 \text{ cm}^3 \approx 0.0055$$

Percentage Conversion:

$$\varphi \approx 0.0055 \times 100\% \approx \mathbf{0.55 \%}$$

5.2.3 Dielectric Results

Starting with the JS sample, a noticeable increase in permittivity at the low frequency (representing big pores) and permittivity dispersion was observed as the sample shifted phases from dry to brine-saturated to CO₂-treated. The higher frequencies in permittivity show the microstructures that the influx and displacement of electrical charge are very minimal to move in, meaning smaller pore sizes. The curvature within the permittivity dispersion curves also increased across these stages. Additionally, the separation between the inlet and outlet permittivity values widened. Electrical conductivity measurements followed a similar trend, showing a significant increase from dry to brine-saturated to CO₂-treated. Conductivity started to increase in the brine-saturated state and the separation between inlet and outlet conductivity values continued.

In the EF shale samples, a progressive increase in permittivity at the low frequency and permittivity dispersion was also observed during each stage. As well as that, the curvature within the permittivity dispersion curves also increased. Additionally, the separation between the inlet and outlet permittivity values widened. However, after CO₂ treatment, this separation was significantly reduced. Conductivity measurements followed a similar trend as the Jordanian sample, and it was further enhanced in the CO₂-treated stage. Although the separation between inlet and outlet conductivity values persisted, it was reduced in the CO₂-treated sample.

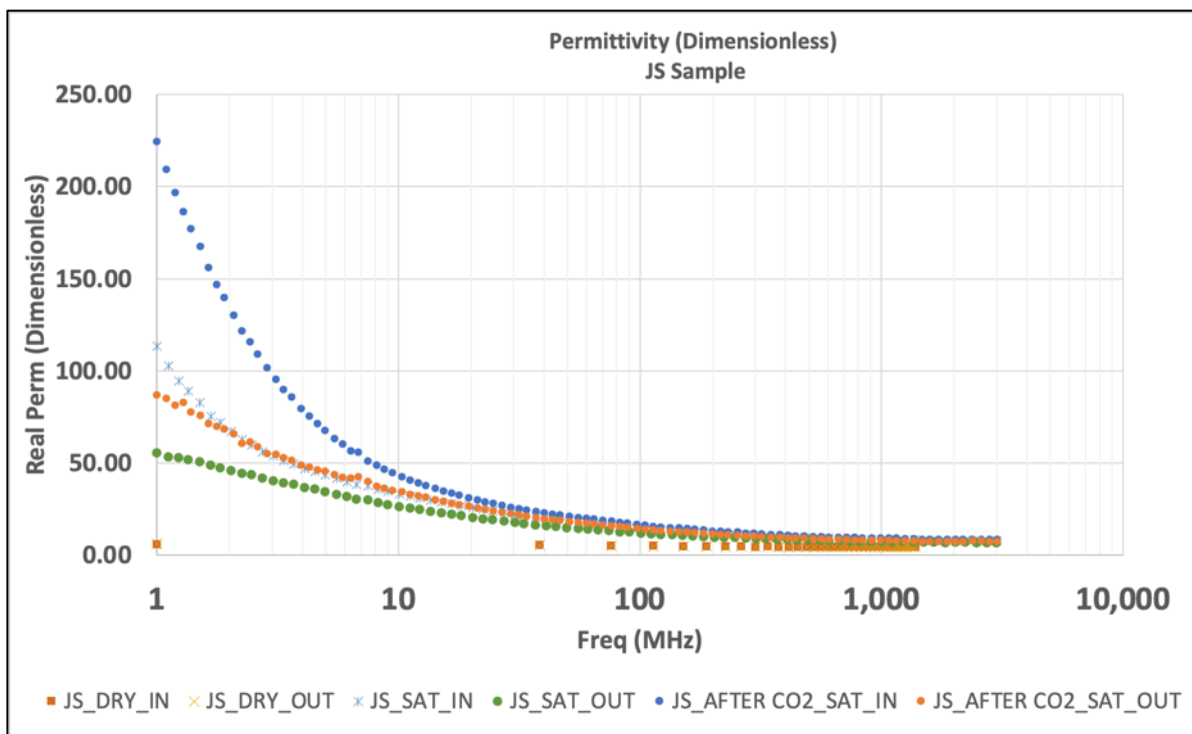


Figure 18. Dielectric Permittivity Data for JS sample

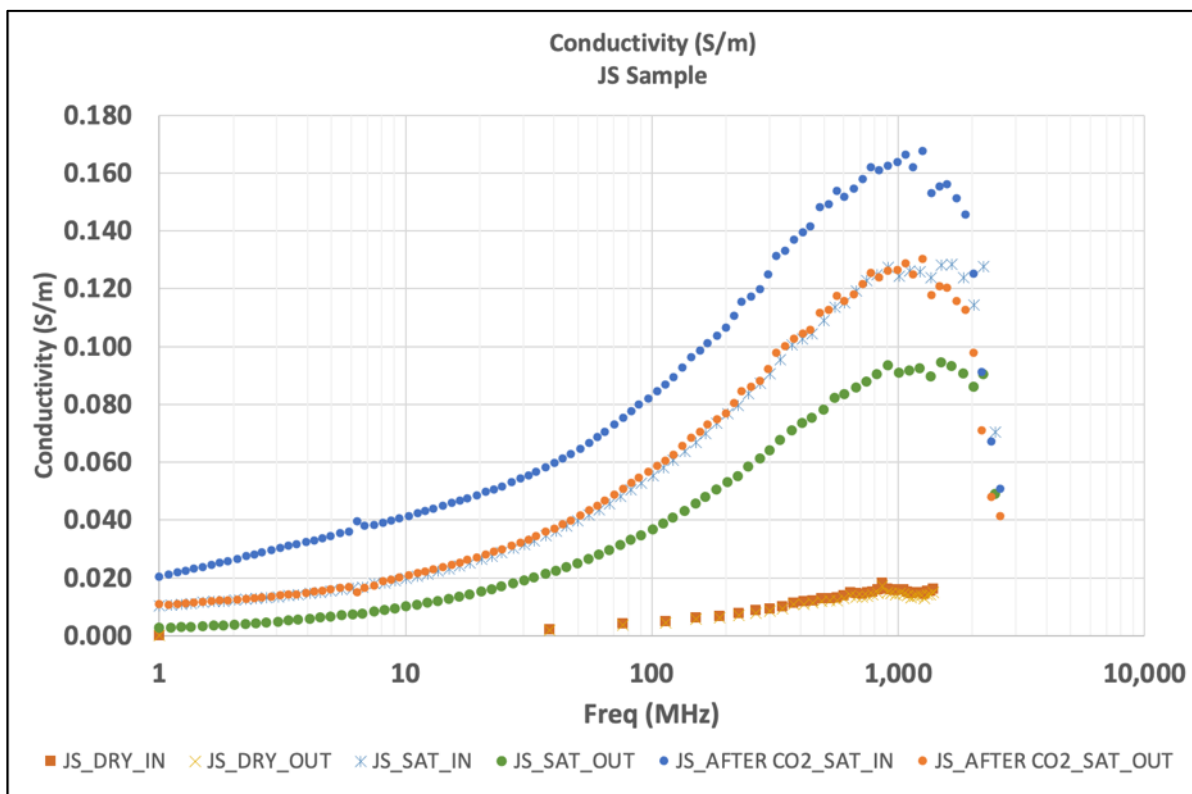


Figure 19. Dielectric Conductivity Data for JS sample

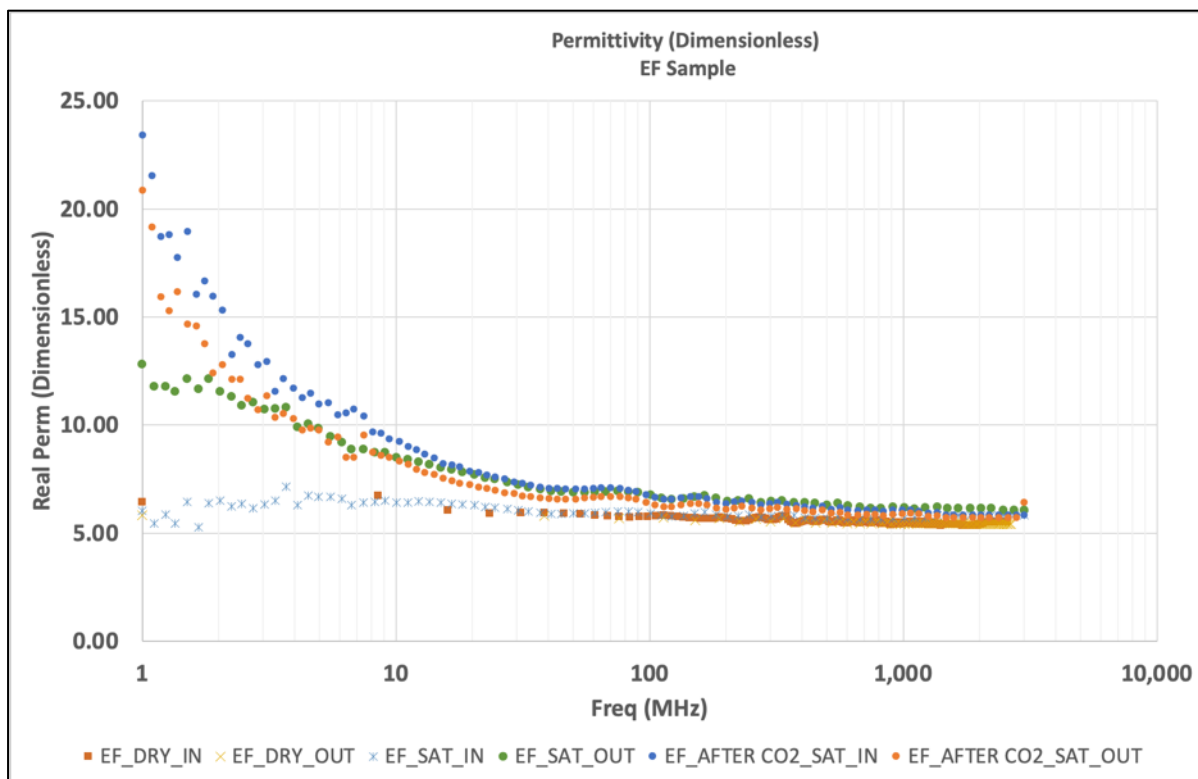


Figure 20. Dielectric Permittivity Data for EF sample

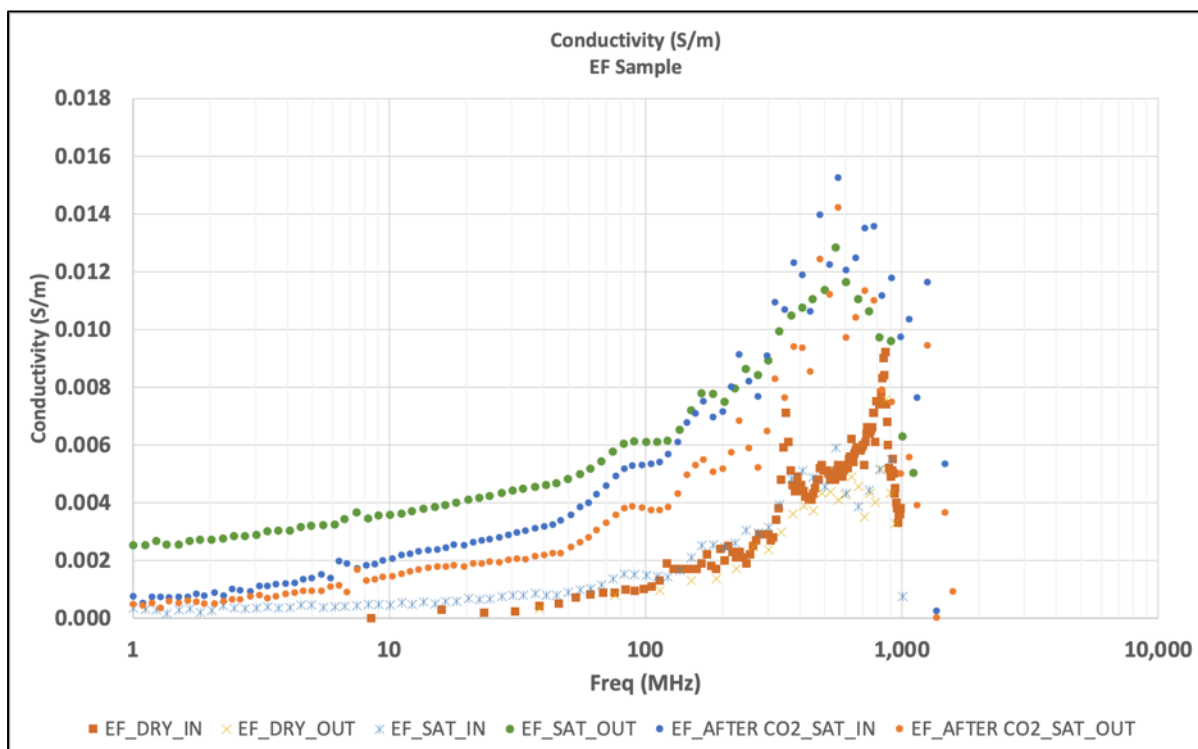


Figure 21. Dielectric Permittivity Data for EF sample

5.3 SEM Images

SEM imaging revealed insights into the microstructures, pore structure and geometry for the samples at their initial none-treated stage, followed by CO₂-treated stage. The samples scale ranges from 100 to 1 micrometer (μm). The SEM images of the none-treated samples demonstrated the initial morphology, microstructure and the pore spaces. Moreover, Initial samples indicated the presence of well-preserved foraminifera. Overall, SEM images for post CO₂-treated chips highlighted sort of “disturbance” of the sample microstructure with some evidence of diagenetic overprinting such as reprecipitation. As well as this, the post CO₂-treated samples revealed a possible enhancement of microfractures, and pores counts. SEM images were analyzed form CO₂-treated core samples sides and center.

5.3.1 JS Samples

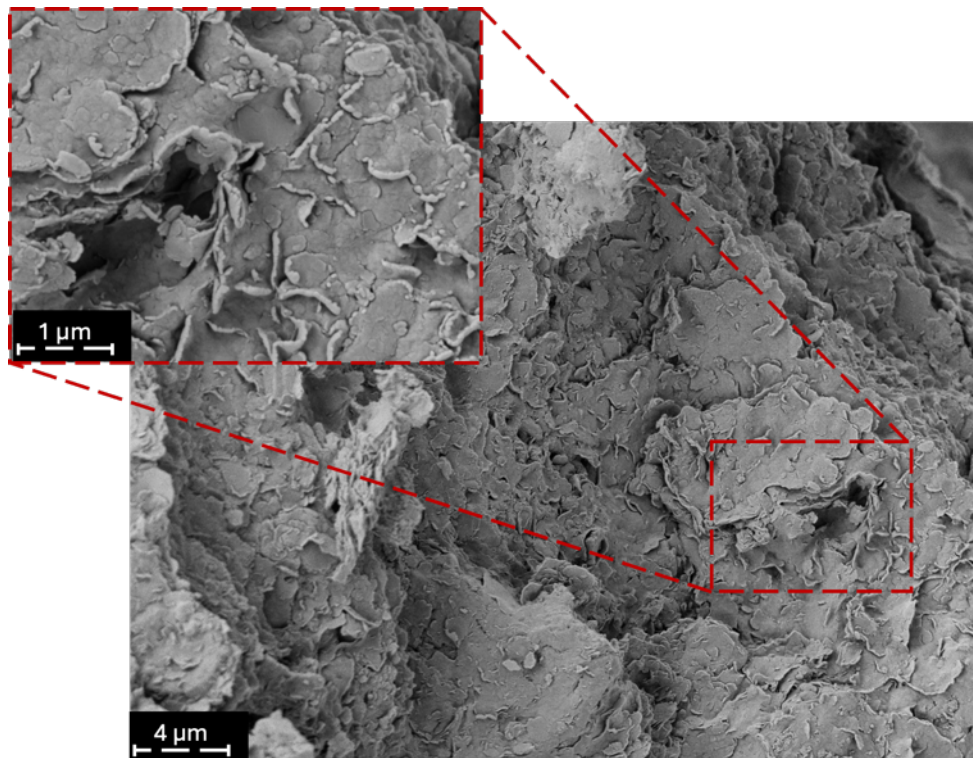


Figure 22. SEM Images for the initial pre-treated stage of JS

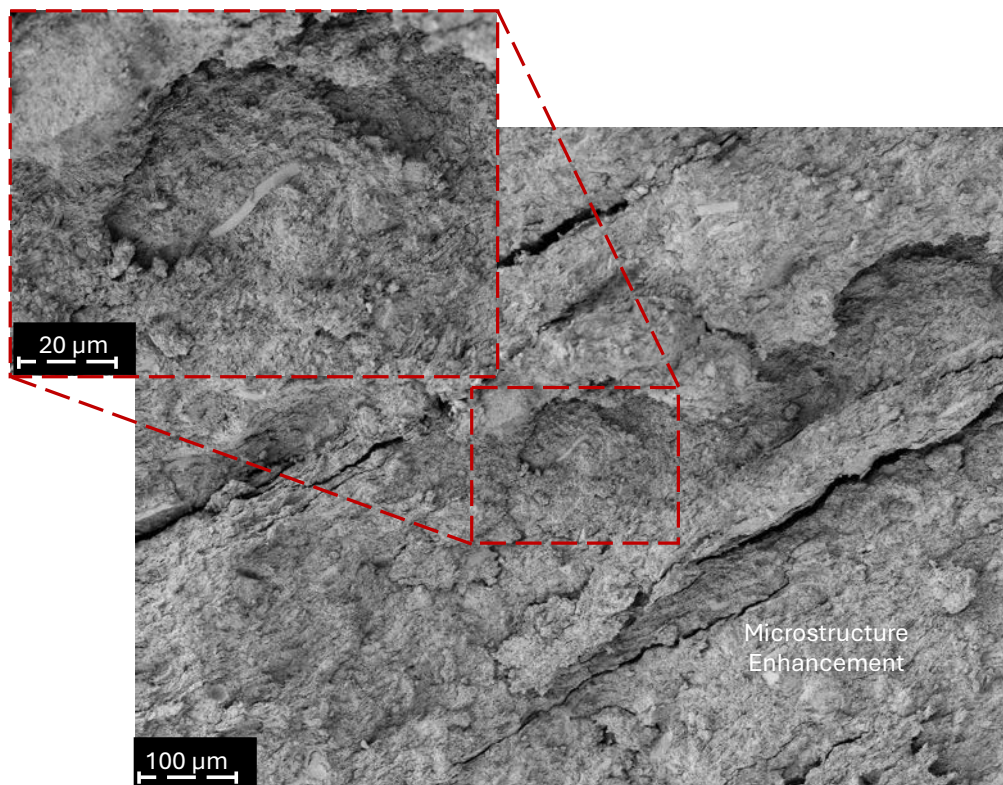


Figure 23. SEM Images for the post CO₂-treated stage of JS core side showing possible microstructure and pore enhancement

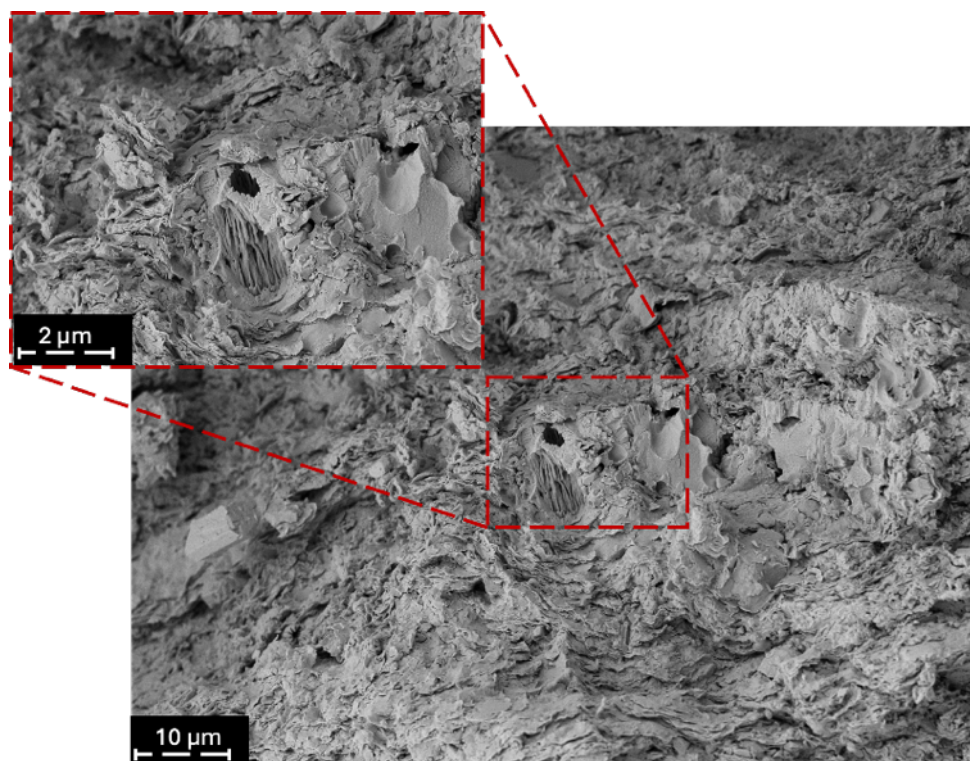


Figure 24. SEM Images for post CO₂-treated stage of JS core center showing diagenetic overprinting

5.3.2 EF samples

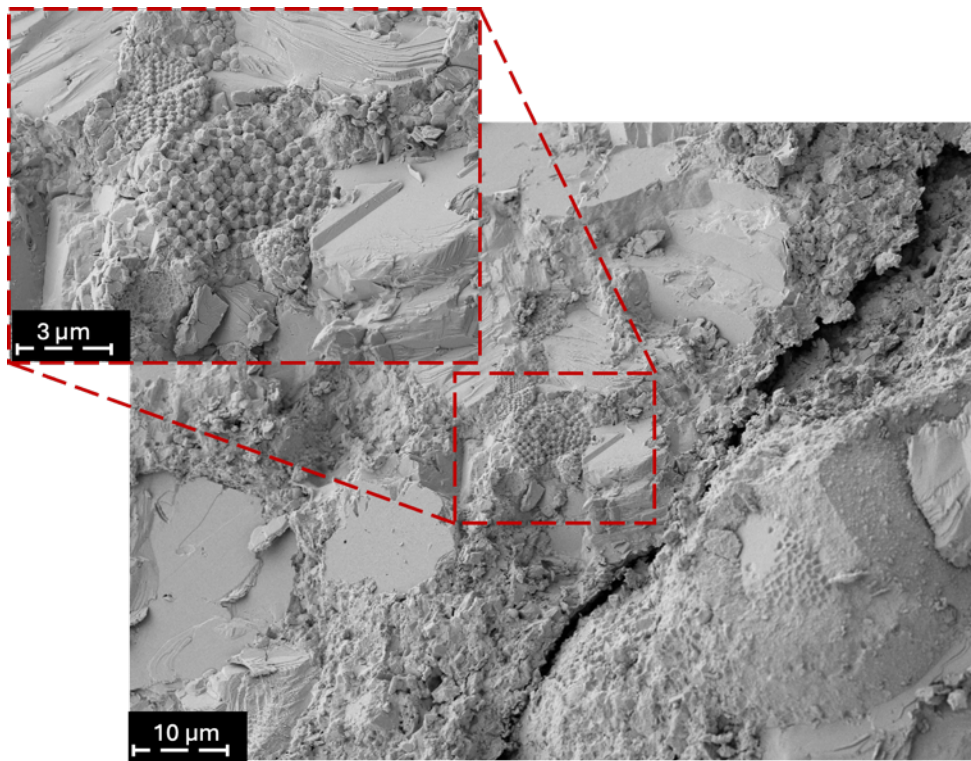


Figure 25. SEM Images for initial pre-treated stage of EF showing a foraminifera foram

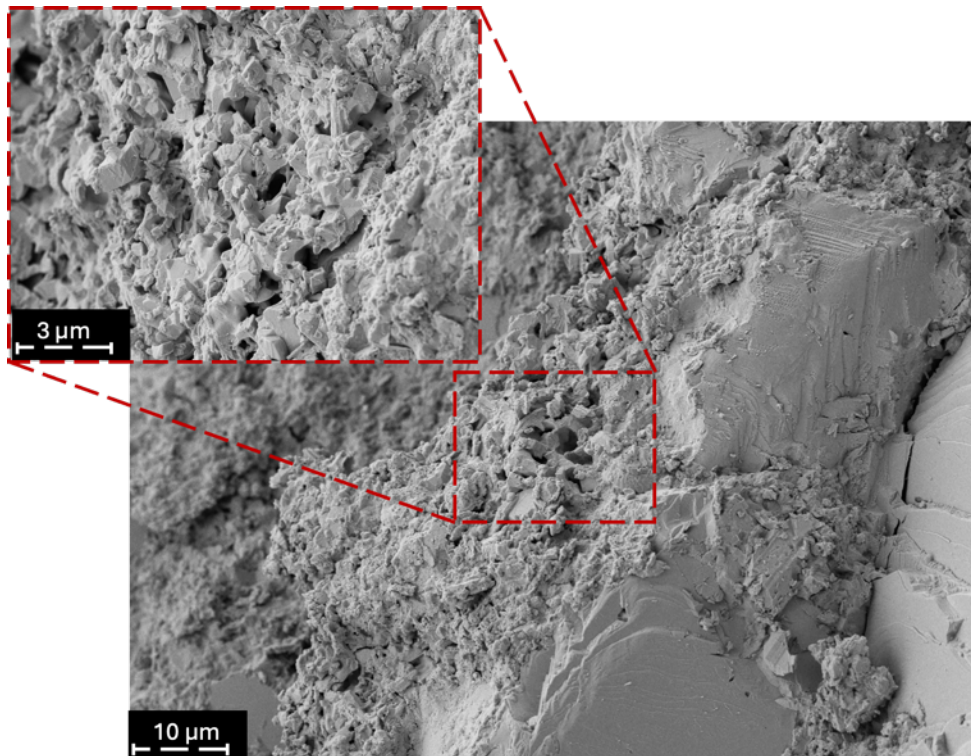


Figure 26. SEM Images for initial pre-treated stage of EF showing microstructures and pores distribution

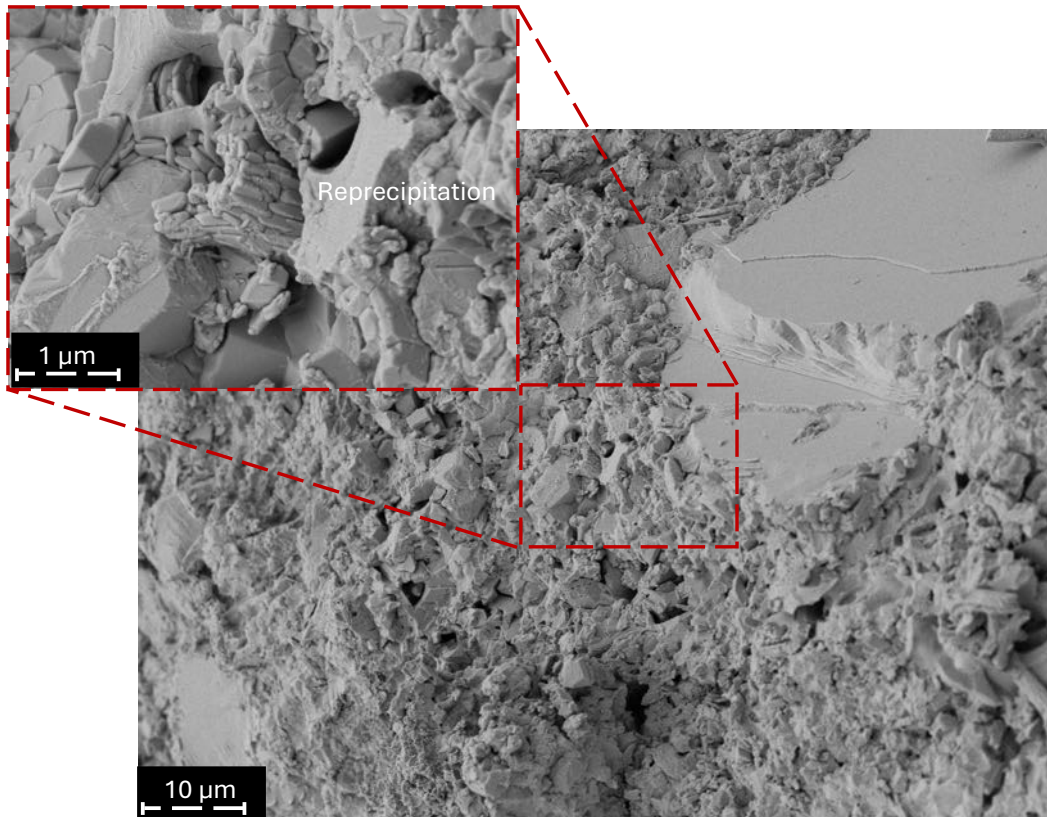


Figure 27. SEM for post CO₂-treated stage of EF core side showing diagenetic overprinting such as reprecipitation

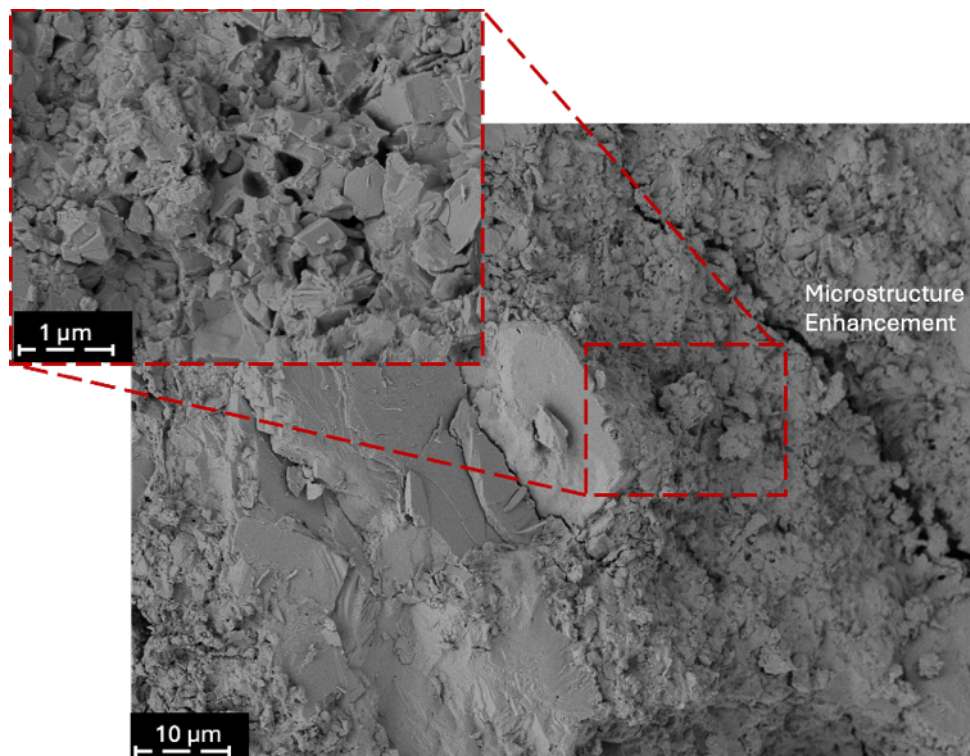


Figure 28. SEM for post CO₂-treated stage of EF core center showing possible microstructure and pores enhancement

5.4 CT Scan

The CT scan analysis provided useful insight in terms of internal structure and density variations within the samples. CT scan results include total of four core samples across the stages examined, which are pre-treatment and post-treatment.

Starting with the pre-treatment JS and EF samples, both samples exhibited relatively uniform density distributions with CT distribution ranging from 1300 to 1500 in JS sample, and from 2200 to 2800 in EF. Initial average densities for JS and EF samples are 2.199 g/cc and 2.293 g/cc respectively. Initial pre-treated samples revealed a clear distinction in terms of density and internal structure.

Post CO₂-treatment sample illustrated density variation across the sample moving from the top to the bottom with wider CT distribution ranging from 1300 to 1600 in JS sample and from 2000 to 2800 in EF. JS sample average densities were reduced to 2.044 g/cc, as well as EF sample with an average of 2.293 g/cc. Finally, the JS sample exhibited a more localized increment of density.

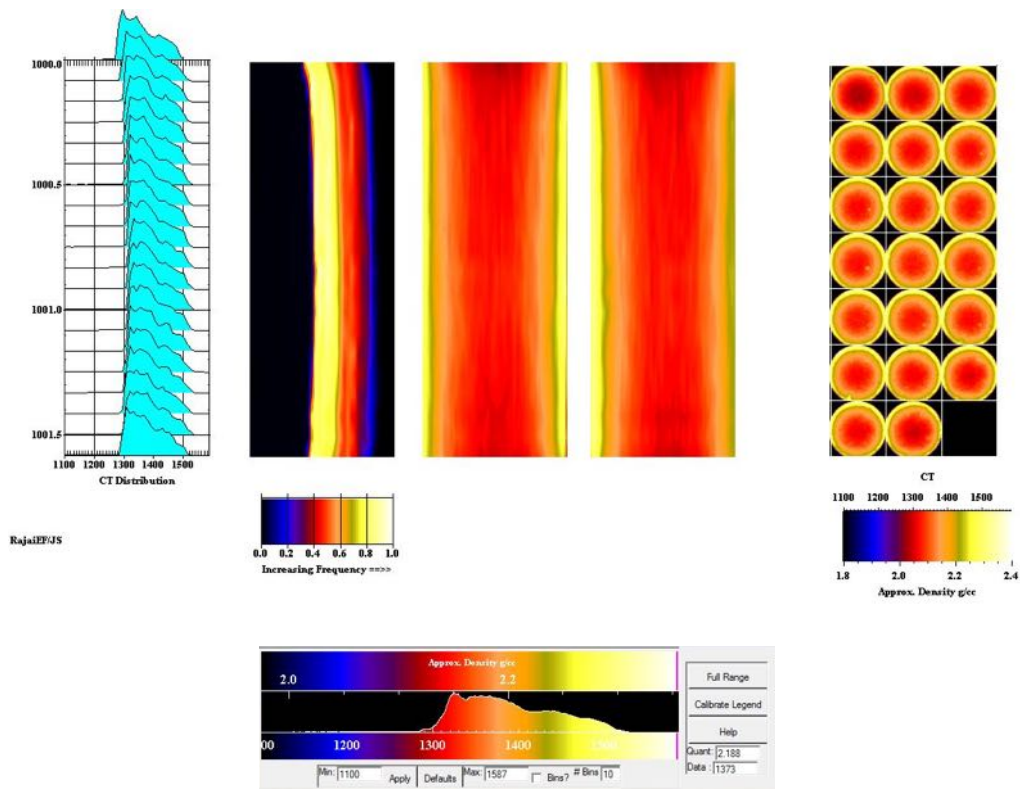


Figure 29. CT scan images of untreated JS sister sample

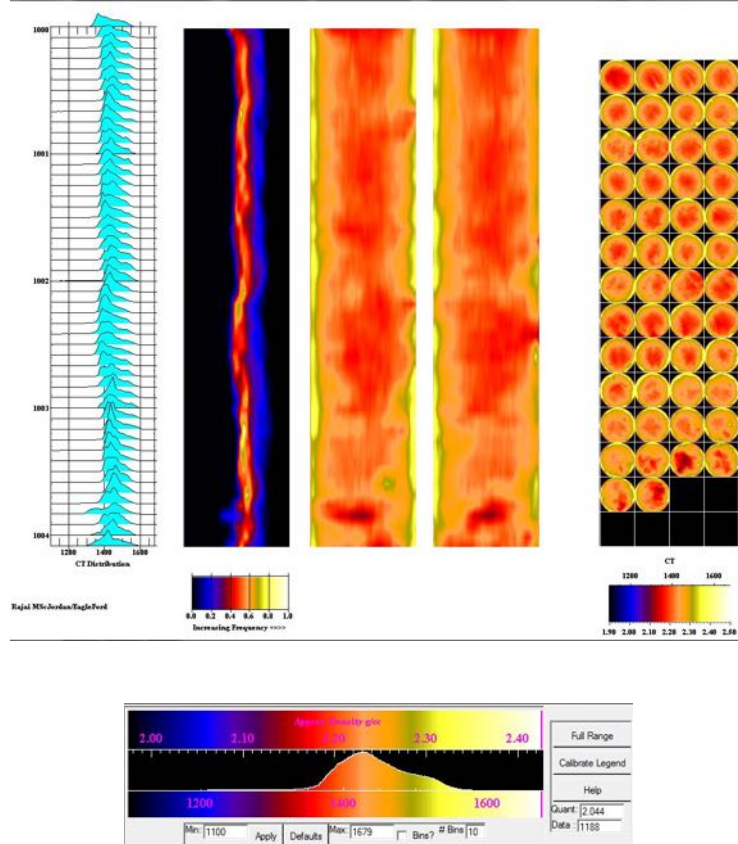


Figure 30. CT scan images of CO₂-treated JS sample

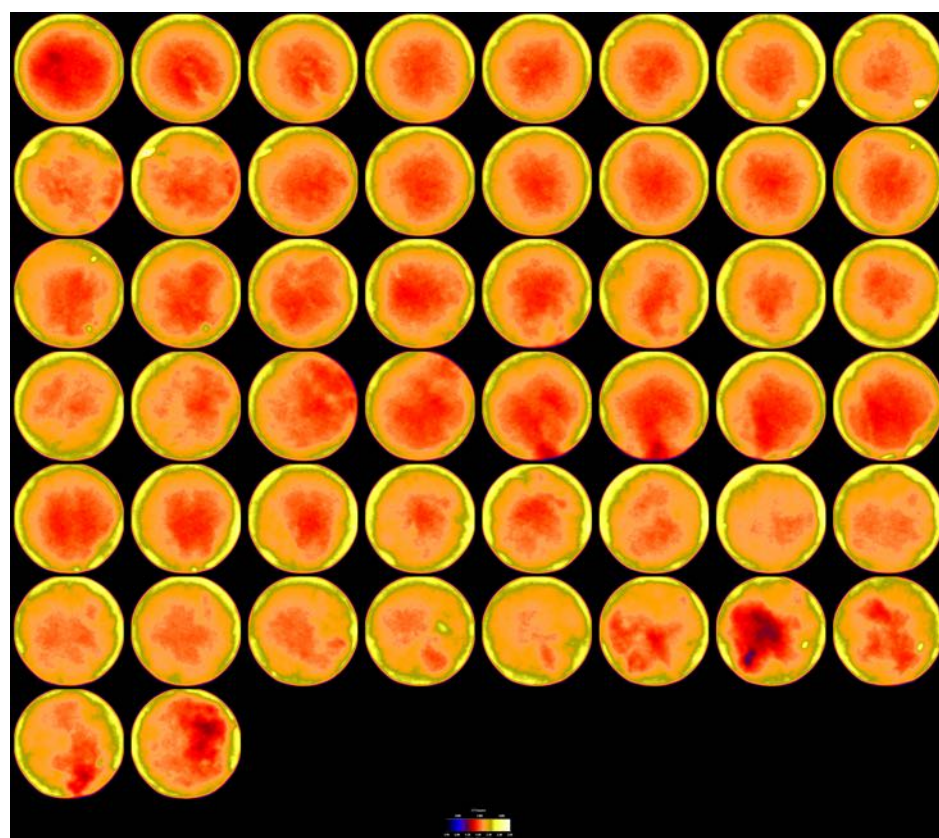
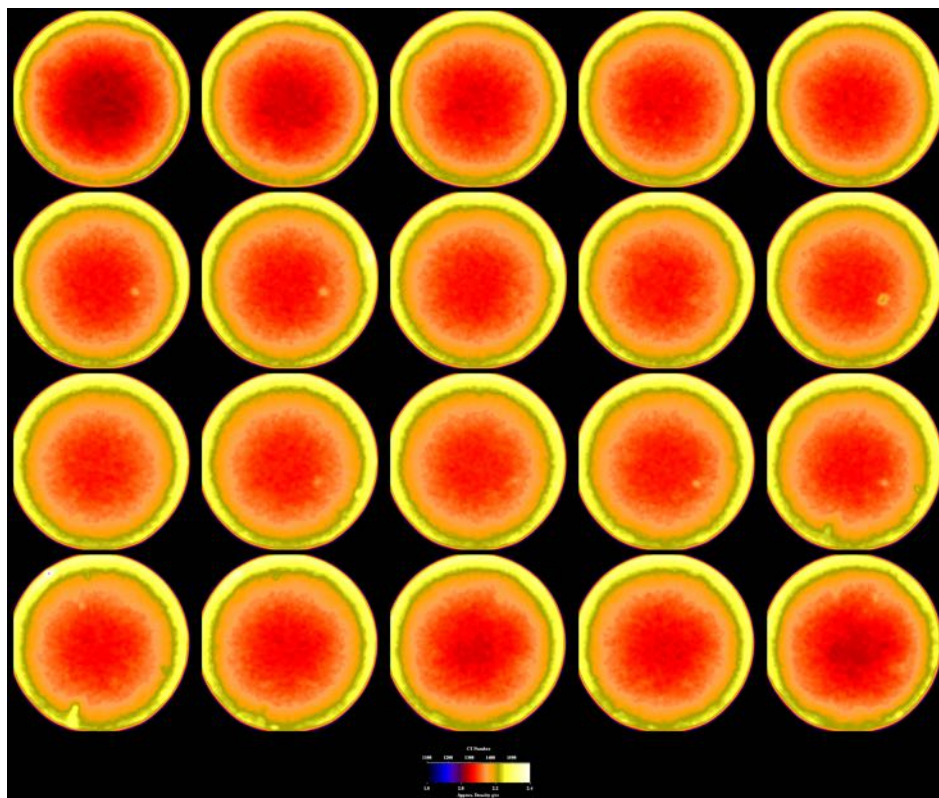


Figure 31. CT scan images of JS samples; non-treated sister sample (top) and CO₂-treated sample (Bottom)

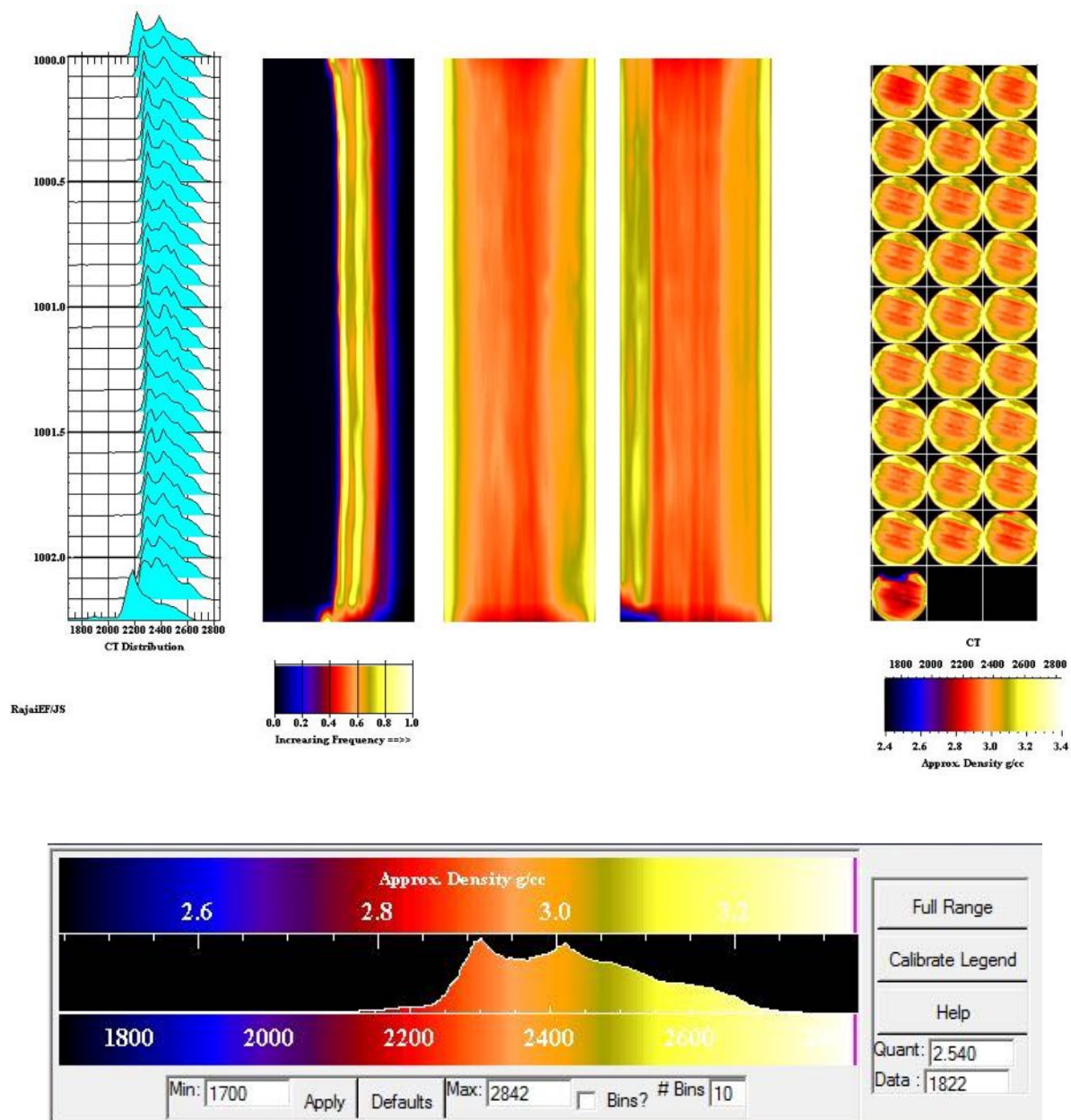


Figure 32. CT scan images of untreated EF sister sample

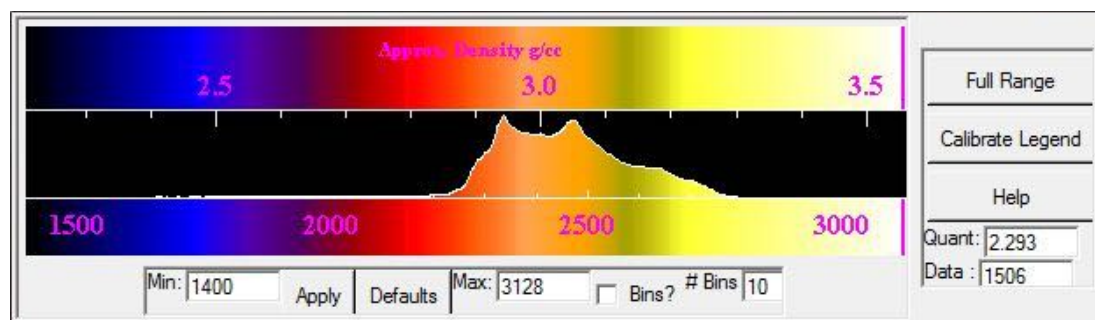
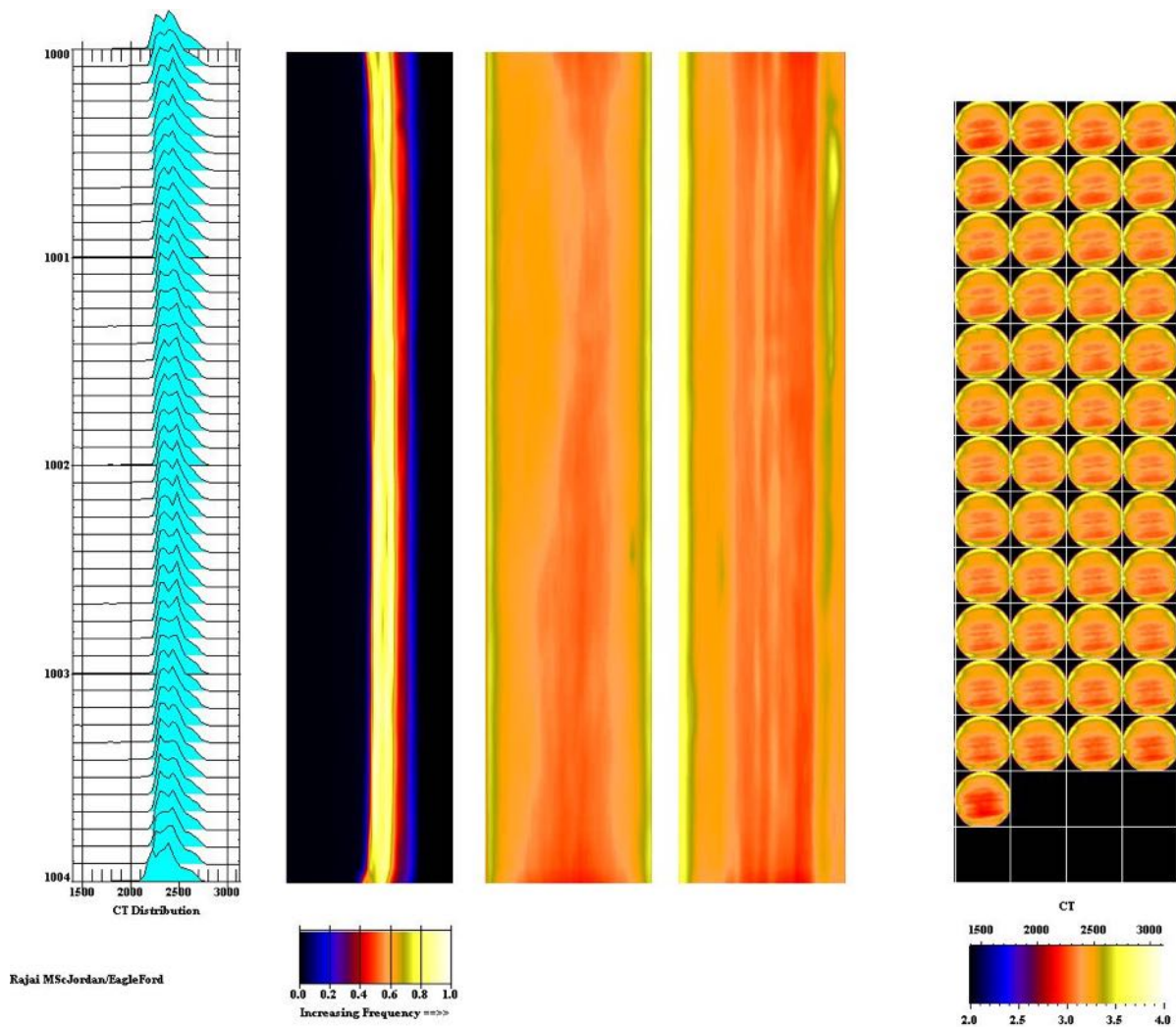


Figure 33. CT scan images of CO₂-treated EF sample

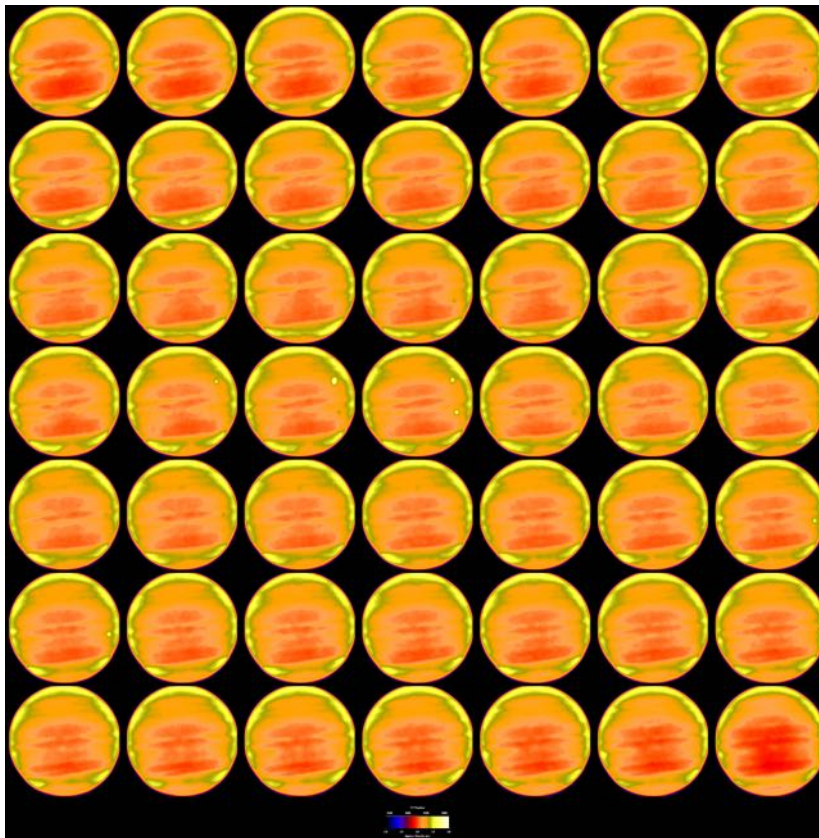
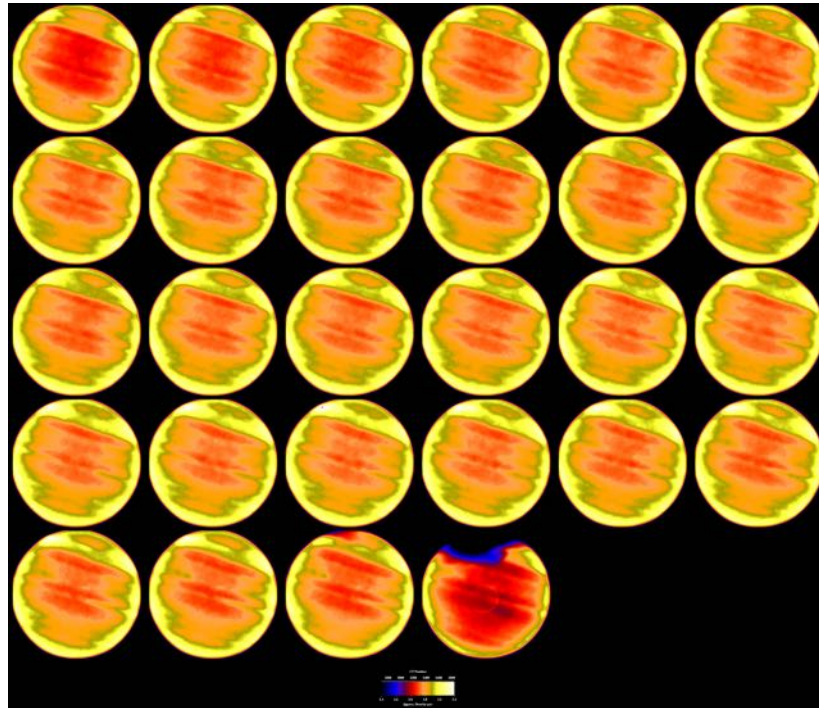


Figure 34. CT scan images of EF samples; non-treated sister sample (Top) and CO₂-treated sample (Bottom)

[CHAPTER 6

DISCUSSION]

Different types of the same set of samples and different CO₂ treatment conditions and artificial maturation were deployed to establish initial base line results on the well characterized Jordanian MCM and Eagle Ford carbonate mudrock formations.

For the powdered samples, conducting CO₂ treatment on -dry and -liquid brine wet samples were to examine the fluid-rock-CO₂ reactions (in liquid brine sample) versus the CO₂-rock reactions (in dry samples). Although, this is considered to be a first to second order chemical reaction, this approach succeeded in capturing variations in the geochemical characteristics under different conditions. Keeping the samples during the CO₂ treatment under a confined pressure of 1300 psi and a controlled temperature of 45 degrees Celsius, was proposed to simulate the dynamic process of subsurface CO₂ sequestration. The workflow unlocked a detailed comparison between the two different conditions in terms of isotopes responses as well as mineralogical and elemental readings, which will be discussed in detail in this chapter.

Petrophysical, SEM and CT scan analysis on core samples demonstrated an overall valuable answer to one of the thesis research questions of investigating the implication of petrophysical analysis on CO₂ treatment in carbonate mudrock samples. Complementing SEM and CT scan on this study was crucial to emphasize the effect of CO₂ treatment on those cores. Both analyses helped on illustrating potential effects in term of the internal structure, microstructure, pore space distribution and geometry, and finally mineral reprecipitation shown in Figures 22-30.

6.1 Pre CO₂-Treatment Sample Characterization

Inorganic geochemical “Mineralogical and Elemental” analysis in Tables 1 and 2 suggest that calcite and Quartz coexisting with moderate to high percentages in both JS and EF samples coincide with the nature of their deposition environment which is shallow-deep marine setting. Quartz could be a product of biomineralization from some types of plankton or diatoms. Moreover, kaolinite presence in the JS sample suggests that kaolinite might originated from the chemical weathering of feldspar-rich rocks, representing early diagenesis and shallow depth of the formation. More confidence of the XRD data was built from the XRF data with fair percentages of aluminum and silicon in the JS sample. XRF data of EF sample showed that calcium was dominant in the sample reflecting the high calcite percentage from XRD.

For source rock characterization from organic geochemical pyrolysis analysis, the analysis can be spilt into three major parts: source rock richness, quality and thermal maturity. JS sample showed high total organic carbon (TOC) of 12.22 TOC%, with quality of type IIS indicated from hydrogen and oxygen indices and sulfur presence (3.25 total sulfur %) (Table 3). This indicates that the sample is deposited in restricted marine settings with influxes of iron as pyrite exists within the sample composition (3% from XRD in Table 1). Furthermore, EF sample has relatively low organic content interpreted by the 3 TOC% with type II kerogen quality. As Figure 15 illustrated, both samples are immature as the T_{max} for both samples are below kerogen type II source rocks common oil window of 435°C. These results contributed significantly to answering whether the samples are the perfect choice for the experiment or not. The results indicated that JS is the organic rich sample, EF is the organic lean sample with 84% calcite (Figure 13), and both of them are immature, hence the artificial maturation for both samples successfully sufficed the comparison needed in this thesis study.

The isotope compositions of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$ in JS and EF pre-treatment samples are examined to understand their initial environmental and diagenetic histories. The $\delta^{13}\text{C}$ values provide insights into the sources and processes of carbon (-5 to +2 ‰ values are representative for sedimentary carbon). Furthermore, Oxygen isotopes ($\delta^{18}\text{O}$) serve as an indication for paleotemperatures and water sources of the samples and finally sulfur isotopes ($\delta^{34}\text{S}$) are used to indicate sulfur origins and microbial activity. JS and EF samples have values of $\delta^{13}\text{C}$ of -1.59 ‰ and -0.78‰ indicating sedimentary carbon. The $\delta^{18}\text{O}$ varied from -2.26‰ in JS to -7.01‰ in EF, suggesting that JS had undergone in less extensive diageneses and burial in comparison to the EF. EF might have formed at relatively higher temperature or undergone through post alteration due to water mixing after precipitation. The variations of $\delta^{34}\text{S}$ values of -5‰ in JS and -18‰ in EF can be interpreted by different sulfur sources and diagenetic conditions experienced on the samples. JS sample indicating a possible marine in origin sulfur reading while the lighter value of $\delta^{34}\text{S}$ in EF could indicate non-marine sulfur sources or reducing environment activity. Moving forward in this chapter, the discussion will be developed to investigate further on isotope responses to CO_2 treatment on the samples.

6.2 Post CO₂-Treatment Characterization

6.2.1 Petrophysical Analysis

a) VP/VS

As indicated by the results, there was an increase in compressional wave after the sample was saturated with brine which is expected because there is an increase in bulk modulus due to the introduction of brine fluid within the sample, which is incompressible compared to air. This was applicable for both, the Jordanian shale and the Eagle Ford samples. Moving forward, the Vp values dropped once the samples were treated with CO₂, with the Jordan shale showing a significant drop which could be due to either bulk modulus gas effect (decreasing bulk modulus) or newly formed fractures. Another factor that can be considered is either the dissolution of calcite was so high (from geochemical analysis study of the same samples), or the layers of the newly formed Kaolinite, which might have created or enhanced the pores causing the drop in compressional velocity.

b) NMR

the results of the NMR after CO₂ treatment indicated a shift in the first major peaks of T2 relaxation time (longer T2 relaxation time) suggesting an enhancement within the pore system and its connectivity which coincides with SEM and CT Scan analysis. The first peak could be related to the matrix pores as low relaxation time originally could indicate smaller pores. Shifting this peak to the left could be an indication of dissolution. The second peak, which could be related to longer pores (fractures or layering of clays), hence more relaxation time will increase the shift, Figure 28 shows microstructure enhancement. However, the increase in the relaxation time is not that pronounced, indicating a smaller enhancement for the layering of clays and fractures. VP/VS and NMR data for both samples suggest that there are no pronounced changes in the samples after CO₂ treatment, indicating no major concern about rock integrity when treated with CO₂.

c) Dielectric

Starting with the Jordanian shale sample, the increase of permittivity when shifting from dry to brine-saturated to CO₂-treated indicates that the introduction of fluids (whether brine or CO₂) accelerated the movement and displacement of charges within the sample. However, the minimum displacement of higher frequencies in permittivity suggests lower fluid content accessibility. Additionally, the curvature dispersion increase indicates pore system complexity which coincides with the CT scan in Figure 30. Possible heterogeneity in the sample was interpreted by the separation of inlet and outlet. Electrical conductivity increments as moving toward the brine-saturated stage is mainly due to the presence of brine-free ions, which facilitated charge movement, and it was even higher in the CO₂-treated stage. This elevated conductivity with CO₂ treatment highlights the enhancement of fluid-rock interactions and pore connectivity. As well as permittivity, the separation between inlet and outlet conductivity values continued, which agrees with the interpreted heterogeneity along the sides of the core.

In the Eagle Ford shale samples, a progressive increase in permittivity at the low frequency demonstrates the same effect that occurred in the Jordanian sample with greater complexity within the pore system interpreted by the permittivity dispersion curvature increase. The heterogeneity in the sample along opposing directions was also interpreted. However, the separation between inlet and outlet conductivity values was reduced in the CO₂-treated sample, indicating a decrease in heterogeneity on the sides of the Eagle Ford shale core sample. CT scan result in Figure 33 shows an overall homogeneous density across the whole Eagle Ford sample. Overall, when comparing the two types of shale, the Jordanian shale exhibited a more pronounced increase in both permittivity and conductivity than the Eagle Ford shale, highlighting a greater sensitivity to fluid saturation and CO₂ treatment. The observations successfully highlighted the impact of fluid saturation and CO₂ treatment on the electrical

properties and pore structure of both samples, with the Jordanian shale sample showing a more pronounced response.

6.2.2 Geochemical Analysis

Mineralogical results illustrated a clear relationship between calcite and liquid brine CO₂ treated samples, as JS showed around 30% drop of its calcite content and EF's calcite dropped by 11% of the total sample. Dry CO₂-treated samples had almost the same calcite composition percentages. This could be explained by the expected calcite dissolution process. Mineral dissolution is interpreted as well from SEM as it was represented by pore size and microstructure enhancement. Quartz on the other hand showed an average 5% increase in mineralogical compositions of the liquid brine samples. Sylvite mineral (KCl) formed during the chemical reactions of the liquid brine CO₂ and shale samples which coincides with the elemental analysis as the increment is clear in potassium and chlorine. Mineral reprecipitation was confirmed from SEM images in Figure 27. Same as calcite, calcium was the only element that showed a clear compositional drop in liquid brine CO₂-treated samples. Overall, post CO₂-treatment carbonate mudrock geochemical properties coincide with what was illustrated on SEM images such as mineral dissolution represented by pore size enhancement, and reprecipitation.

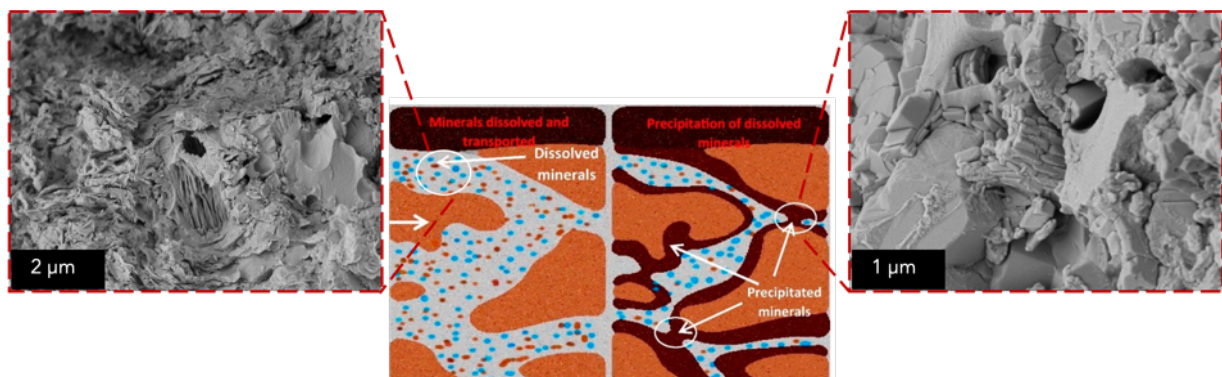


Figure 35. Dissolution and precipitation processes during CO₂ injection (Li et al. 2022), which agrees with the thesis SEM results from Figures 24 and 27

6.3 Influence of Organic Richness and Maturity Variations on Stable Isotope Ratios for pre- and post-CO₂-Treated Samples

6.3.1 Sulfur Isotope Ratios

$\delta^{34}\text{S}$ values of the immature samples showed an interesting divergent trend. The $\delta^{34}\text{S}$ of JS exhibited lighter values in the dry and liquid brine samples (total of -4‰ from JS-pre to JS-LB), while EF showed heavier $\delta^{34}\text{S}$ readings with around 6‰ from EF-pre to liquid brine CO₂ saturated samples. What is worth noticing is that $\delta^{34}\text{S}$ values responded even to the dry CO₂-treated samples, indicating that CO₂-rock interaction affected the $\delta^{34}\text{S}$ values even at low concentrations of the sulfur element (sulfur is only 1.6 % in EF). A possible interpretation of the divergent trend phenomena would be the fact that the origin of sulfur and diagenesis on both samples are different, as well as their organic richness, initial maturity variation, and distinct organic macerals residing in those kerogens.

6.3.2 Carbon Isotope Ratios

Starting with the Immature samples, $\delta^{13}\text{C}$ values illustrated ¹³C depletion with the values being isotopically lighter by 2.4‰ in JS and 1.4‰. both samples suggest that the liquid brine CO₂ treated samples have more effect on $\delta^{13}\text{C}$ values. The $\delta^{13}\text{C}$ isotope shift in the immature JS dry CO₂ treated sample is almost negligible with isotope values being isotopically lighter by 0.033‰. On the other hand, $\delta^{13}\text{C}$ isotope shift in the immature EF dry CO₂ treated sample is relatively higher with isotope values being isotopically lighter by 0.55‰.

Interestingly, and in contradiction with what was noticed in the immature samples about ¹³C depletion in the liquid brine CO₂ treated samples. Both mature JS and EF liquid brine CO₂ treated samples showed minor depletion of $\delta^{13}\text{C}$ with 0.174‰ shift on the mature JS liquid brine CO₂ treated sample and 0.11‰ shift on the mature EF liquid brine CO₂ treated sample.

Given the fact that the liquid brine used has the same chemical formula in both the immature and mature samples, maturity variations could contribute significantly to $\delta^{13}\text{C}$ isotope readings.

The $\delta^{13}\text{C}$ isotope shift in the mature JS and EF dry CO_2 treated samples were 0.24‰ for JS and 0.09‰ for EF.

6.3.3 Oxygen Isotope Ratios

For the immature samples, $\delta^{18}\text{O}$ values depicted an interesting distinct pattern in terms of their response to the dry CO_2 treatment. Dry CO_2 treated $\delta^{18}\text{O}$ values are heavier in JS by 0.54‰, yet EF results show the opposite as EF-dry samples exhibit 0.37‰ lighter $\delta^{18}\text{O}$. This could be because of the different mineral compositions of the samples. Moreover, mature dry CO_2 -treated samples showed the same pattern for JS with 0.24‰ enrichment. Mature EF dry CO_2 treated samples exhibit 0.05‰ $\delta^{18}\text{O}$ enrichment.

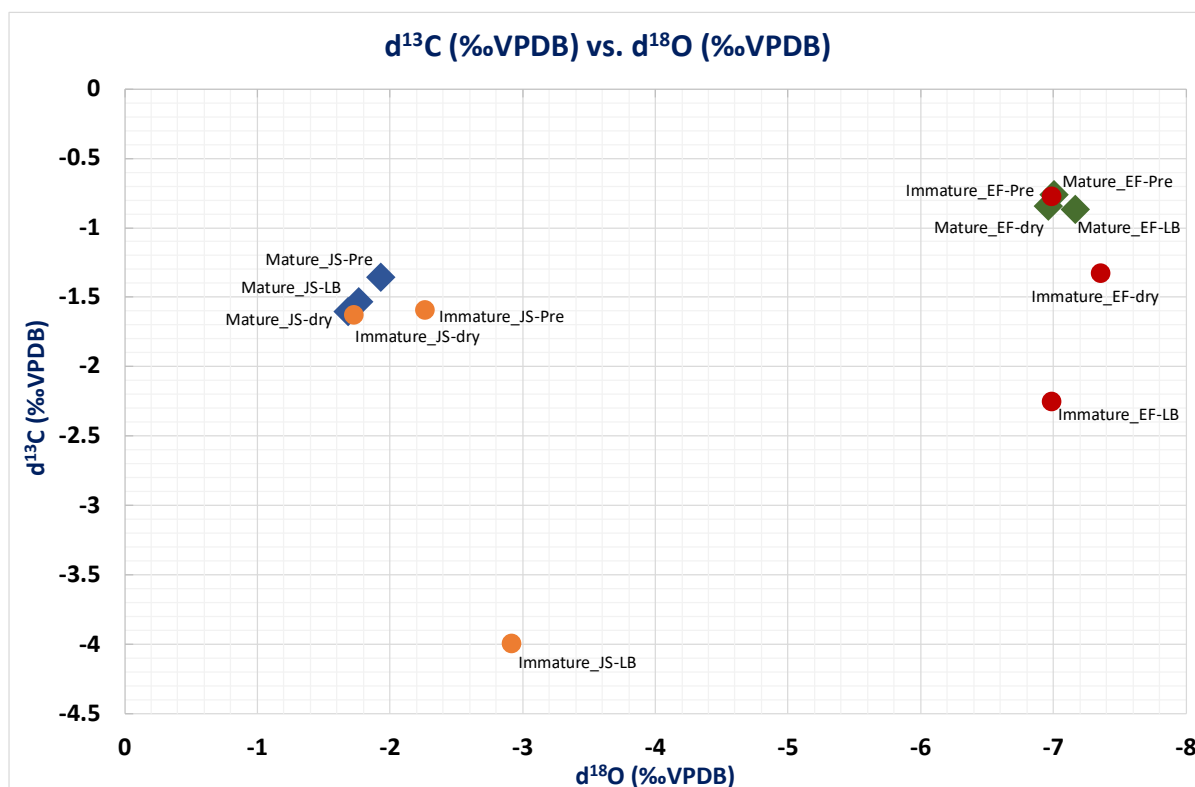


Figure 36. Plot for $\delta^{13}\text{C}$ (‰VPDB) vs. $\delta^{18}\text{O}$ (‰VPDB) isotopes for all samples showing the shift differences between both samples as well as their maturity stage. it is well noticed that Immature JS-LB scores the biggest carbon isotope shift

6.3.4 Stable Isotope Fractionation

As discussed in the literature, usually different physical and chemical behaviors of isotopes will lead to isotopic fractionation effects hence this will give an isotopic shift in their values. The interest in carbon and oxygen isotopic shifts in this study is because both coexist in both reactants; CO_2 and in carbonate systems as the general calcium carbonate chemical formula is CaCO_3 . Nevertheless, when introducing organic matter to the system, the molecular complexity of the kerogen (Figure 37) will play a substantial role in the kinetic isotope effect during the chemical reactions.

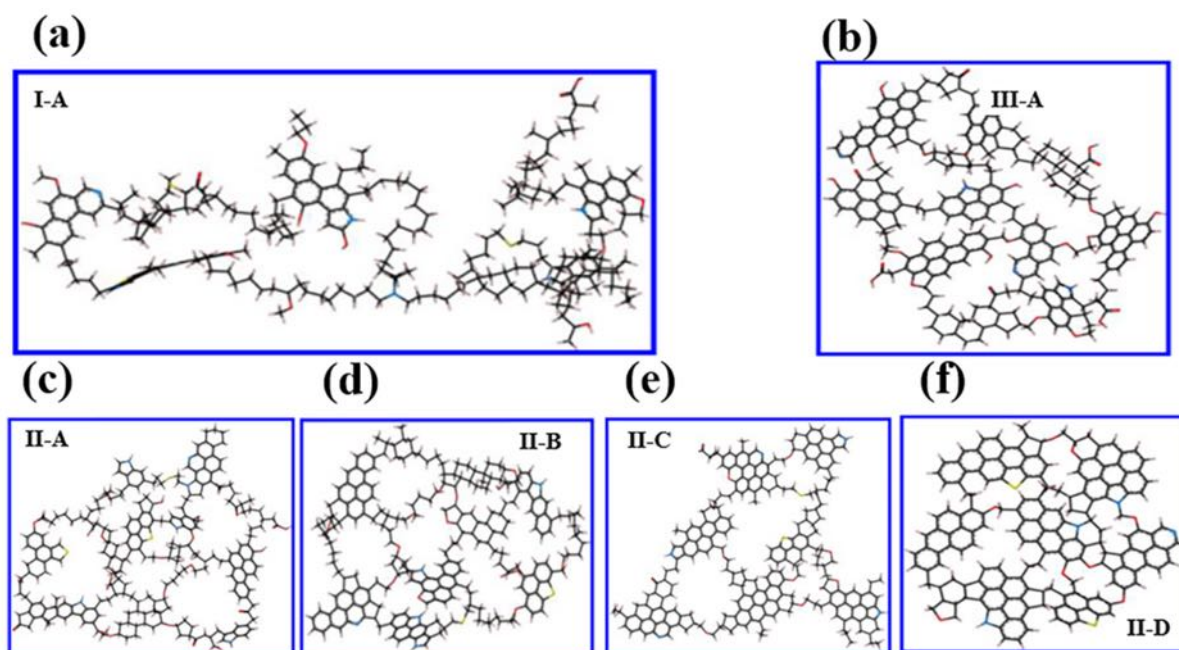


Figure 37. An illustration of variable chemical formula for each kerogen types (Sun et al., 2023).

Isotope enrichment and depletion in this empirical thesis can be interpreted by the fact that heavy isotopes tend to favor the stronger element chemical bonds (Bigeleisen,1965). In this thesis study, the isotope results showed insightful interpretation that kerogen existence as well as thermal maturity may result in different isotope ratios when carbonate mudrock is treated with CO₂. Further detailed organic geochemistry, such as fingerprinting and biomarker analysis, is advised to be done to investigate the precise effect of kerogen types on isotope shifts, which is beyond the scope of this thesis study. Nevertheless, the pronounced carbon isotope shifts in both immature samples coincide with the fact of the availability of organic matter in the samples.

In this laboratory experiment, CO₂ was introduced to the sample with confined pressure with constant temperature and for a certain period. This makes the possibility of the isotope portioning due to the equilibrium effect, i.e., first to second-order chemical reaction. Which was interpreted by mineral dissolution and reprecipitation. Thereupon, CO₂ sequestration in the subsurface with carbonate mudrock formations will theoretically result in isotope shifts which could be recorded by reading isotopic values systematically.

[CHAPTER 7

CONCLUSION]

This thesis explored the implications of analyzing isotopic responses, alongside geochemical and petrophysical analyses, concerning CO₂ treatment in carbonate mudrock samples. Beginning with the geochemical analysis, the study interpreted mineral dissolution, which was corroborated by scanning electron microscopy (SEM), demonstrating enhanced pore size. Additionally, mineral reprecipitation was confirmed through inorganic geochemical analysis and visual evidence from SEM images.

In the context of petrophysical analysis and computed tomography (CT) scanning, the results indicated a drop in velocity (VP) after CO₂ treatment, with a more pronounced decrease observed in the Jordanian shale sample. This reduction is attributed to several factors, including the bulk modulus gas effect (which decreases bulk modulus), the formation of new fractures, or the dissolution of calcite. Furthermore, there was an increase in T₂ relaxation time, permittivity, and electrical conductivity following CO₂ treatment. These changes suggest enhanced dissolution, an improved pore system, increased connectivity, and the creation of new fractures within the rock. Overall petrophysical data for both samples suggest that there are no pronounced changes in the samples after CO₂ treatment, indicating no major concern about rock integrity when treated with CO₂.

Lastly, the isotopic analysis revealed that different isotopes exhibited varying shifts in response to CO₂ treatment with dry and liquid brine. These distinct responses are interpreted as being influenced by variations in organic richness and thermal maturity, and the diagenetic processes that the source rock has undergone. Finally, the pronounced carbon isotope shifts in both immature samples coincide with the fact of the availability of organic matter in the samples.

References

- [1] ABOUSSOU, A. (2016). New Rock-Eval method for Pyritic and Organic Sulphur quantification: Application to study Organic Matter preservation in Jurassic sediments. [Doctoral thesis in Geosciences, Sorbonne Universit].
- [2] Abu-Mahfouz, I. S. (2022). Geochemical and Petrographic Characteristics of Lithofacies from Upper Cretaceous Organic-Rich Source Rocks, Jordan. IPTC-21914-MS. <https://doi.org/10.2523/IPTC-21914-MS>
- [3] Abu-Mahfouz, I. S., & Et al. (2019). Genesis and role of bitumen in fracture development during early catagenesis. *Petroleum Geoscience*. <https://doi.org/10.1144/petgeo2018-179>
- [4] Bigeleisen, J. (1965). Chemistry of Isotopes. *Science*, 147(3657), 463–471. <https://doi.org/10.1126/science.147.3657.463>
- [5] Cheng, Q., Tang, J., Liu, Y., Jia, Y., Lu, Y., Sun, X., Zhao, G., & Liu, Y. (2024). Pore alteration of Yanchang shale after CO₂-brine-rock interaction: Influence on the integrity of caprock in CO₂ geological sequestration. *Fuel*, 363, 130952. <https://doi.org/10.1016/j.fuel.2024.130952>
- [6] Dielectric Permittivity — GPG 0.0.1 documentation. (n.d.). https://gpg.geosci.xyz/content/physical_properties/physical_properties_dielectric_permittivity.html
- [7] Faure, G., & Mensing, T. M. (2005, January 1). *Isotopes*. John Wiley & Sons
- [8] Goodman, A., Fukai, I., Dilmore, R., Frailey, S., Bromhal, G., Soeder, D., Gorecki, C., Peck, W., Rodosta, T., & Guthrie, G. (2014). Methodology for assessing CO₂ storage potential of organic-rich shale formations. *Energy Procedia*, 63, 5178–5184. <https://doi.org/10.1016/j.egypro.2014.11.548>
- [9] Hakimi, M. H., & Et al. (2018). Pyrolysis analyses and bulk kinetic models of the Late Cretaceous oil shales T in Jordan and their implications for early mature sulphur-rich oil generation potential. *Marine and Petroleum Geology*. <https://doi.org/10.1016/j.marpetgeo.2018.01.036>
- [10] Hakimi, M. H., Abdullah, W. H., Alqudah, M., Makeen, Y. M., & Mustapha, K. A. (2016). Organic geochemical and petrographic characteristics of the oil shales in the Lajjun area, Central Jordan: Origin of organic matter input and preservation conditions. *Fuel*, 181, 34–45. <https://doi.org/10.1016/j.fuel.2016.04.070>
- [11] Hassan, A., Elsayed, M., Oshaish, A., Al-Ofi, S., El-Husseiny, A., Abu-Mahfouz, I. S., Mahmoud, M., Abouelresh, M., & Attia, H. (2024). Evaluating the impact of artificial

maturation on the petrophysical and geochemical properties of unconventional shale formations by integrating dielectric and NMR measurements. *International Journal of Coal Geology*, 285, 104492. <https://doi.org/10.1016/j.coal.2024.104492>

- [12] Hazarika, S., Boruah, A., & Kumar, H. (2023). Study of pore structure of shale formation for CO₂ storage. *Materials Today: Proceedings*. <https://doi.org/10.1016/j.matpr.2023.06.014>
- [13] Hou, L., Zou, C., Yu, Z., Luo, X., Wu, S., Zhao, Z., Lin, S., Yang, Z., Zhang, L., Wen, D., & Cui, J. (2021, November). Quantitative assessment of the sweet spot in marine shale oil and gas based on geology, engineering, and economics: A case study from the Eagle Ford Shale, USA. *Energy Strategy Reviews*, 38, 100713. <https://doi.org/10.1016/j.esr.2021.100713>
- [14] Humez, P., Négrel, P., Lagneau, V., Lions, J., Kloppmann, W., Gal, F., Millot, R., Guerrot, C., Flehoc, C., Widory, D., & Girard, J. F. (2014, March). CO₂–water–mineral reactions during CO₂ leakage: Geochemical and isotopic monitoring of a CO₂ injection field test. *Chemical Geology*, 368, 11–30. <https://doi.org/10.1016/j.chemgeo.2014.01.001>
- [15] Humez, P., Négrel, P., Lagneau, V., Lions, J., Kloppmann, W., Gal, F., Millot, R., Guerrot, C., Flehoc, C., Widory, D. and Girard, J.F., 2014. CO₂–water–mineral reactions during CO₂ leakage: Geochemical and isotopic monitoring of a CO₂ injection field test. *Chemical Geology*, 368, pp.11-30.
- [16] Izadpanahi, A., Blunt, M.J., Kumar, N., Ali, M., Tassinari, C.C.G. and Sampaio, M.A., 2024. A review of carbon storage in saline aquifers: Mechanisms, prerequisites, and key considerations. *Fuel*, 369, p.131744.
- [17] Kalam, S., Olayiwola, T., Al-Rubaii, M.M., Amaechi, B.I., Jamal, M.S. and Awotunde, A.A., 2021. Carbon dioxide sequestration in underground formations: review of experimental, modeling, and field studies. *Journal of Petroleum Exploration and Production*, 11, pp.303-325.
- [18] Konhauser, K. (2007). *Introduction to geomicrobiology*. Blackwell Publishing.
- [19] Li, L., Zhang, X., Liu, J., Xie, Q., Zhou, X., Zheng, J., & Su, Y. (2022). Research Progress and Prospect of Carbon Dioxide Utilization and Storage Based on Unconventional Oil and Gas Development. *Energies*, 15(24), 9383. <https://doi.org/10.3390/en15249383>
- [20] Lu, T., Zeng, K., Jiang, P., Zhou, B., & Xu, R. (2022). Competitive adsorption in CO₂ enhancing shale gas: Low- field NMR measurement combined with molecular simulation for selectivity and displacement efficiency model. *Chemical Engineering Journal*, 440, 135865. <https://doi.org/10.1016/j.cej.2022.135865>

- [21] Lüning, S., & Kuss, J. (2014). Petroleum Geology of Jordan. The American Association of Petroleum Geologists., AAPG Memoir, 217-239. <https://doi.org/10.1036/13431858M1063607>
- [22] Murugesu, M. P., Joewondo, N., & Prasad, M. (2023, March). Carbon storage capacity of shale formations: Mineral control on CO₂ adsorption. *International Journal of Greenhouse Gas Control*, 124, 103833. <https://doi.org/10.1016/j.ijggc.2023.103833>
- [23] Myrntinen, A., Becker, V., van Geldern, R., Würdemann, H., Morozova, D., Zimmer, M., Taubald, H., Blum, P., & Barth, J. (2010, December). Carbon and oxygen isotope indications for CO₂ behaviour after injection: First results from the Ketzin site (Germany). *International Journal of Greenhouse Gas Control*, 4(6), 1000–1006. <https://doi.org/10.1016/j.ijggc.2010.02.005>
- [24] Myrntinen, A., Jeandel, E., Ukelis, O., Becker, V., van Geldern, R., Blum, P., & Barth, J. (2012, August). Stable carbon isotope techniques to quantify CO₂ trapping under pre-equilibrium conditions and elevated pressures and temperatures. *Chemical Geology*, 320–321, 46–53. <https://doi.org/10.1016/j.chemgeo.2012.05.008>
- [25] Ratcliffe, K., Wright, A., & Schmidt, K. (2012). Application of inorganic whole-rock geochemistry to shale resource plays: an example from the Eagle Ford Shale Formation, Texas. *The Sedimentary Record*, 10(2), 4–9. <https://doi.org/10.2110/sedred.2012.2.4>
- [26] Rosso, J. J. (2013, January 1). FROM THE SERIES EDITOR. *Reviews in Mineralogy and Geochemistry*, 77(1), iii–iii. <https://doi.org/10.2138/rmg.2013.77>.
- [27] Selley, R. C., & Sonnenberg, S. A. (2014, November 8). *Elements of Petroleum Geology*. Academic Press.
- [28] Serno, S., Flude, S., Johnson, G., Mayer, B., Karolytè, R., Haszeldine, R. S., & Gilfillan, S. M. (2017, August). Oxygen isotopes as a tool to quantify reservoir-scale CO₂ pore-space saturation. *International Journal of Greenhouse Gas Control*, 63, 370–385. <https://doi.org/10.1016/j.ijggc.2017.06.009>
- [29] Serno, S., Flude, S., Johnson, G., Mayer, B., Karolytè, R., Haszeldine, R. S., & Gilfillan, S. M. (2017, August). Oxygen isotopes as a tool to quantify reservoir-scale CO₂ pore-space saturation. *International Journal of Greenhouse Gas Control*, 63, 370–385. <https://doi.org/10.1016/j.ijggc.2017.06.009>
- [30] Sharp, Z. (2007, January 1). *Principles of Stable Isotope Geochemistry*. Prentice Hall.
- [31] Sun L, Liu Y, Cheng Z, Jiang L, Lv P, Song Y. Review on multiscale CO₂ mineralization and geological storage: mechanisms, characterization, modeling, applications and perspectives. *Energy & Fuels*. 2023 Aug 24;37(19):14512-37.
- [32] Sun, S., Liang, S., Liu, Y., Liu, D., Gao, M., Tian, Y., & Wang, J. (2023). A review on shale oil and gas characteristics and molecular dynamics simulation for the fluid

behavior in shale pore. *Journal of Molecular Liquids*, 376, 121507.
<https://doi.org/10.1016/j.molliq.2023.121507>

- [33] Usman, M., Grohmann, S., Abu-Mahfouz, I. S., Vahrenkamp, V., & Littke, R. (2024). Effects of geochemical compositional heterogeneities on hydrocarbon expulsion and thermal maturation: An analog study of Maastrichtian source rocks from Jordan. *International Journal of Coal Geology*, 294, 104587.
<https://doi.org/10.1016/j.coal.2024.104587>
- [34] Wang, J., Wang, K., Shan, X., Taylor, K. G., & Ma, L. (2024, February). Potential for CO₂ storage in shale basins in China. *International Journal of Greenhouse Gas Control*, 132, 104060. <https://doi.org/10.1016/j.ijggc.2024.104060>
- [35] Wang, Y., Dai, Z., Chen, L., Shen, X., Chen, F., & Soltanian, M. R. (2023, February). An integrated multi- scale model for CO₂ transport and storage in shale reservoirs. *Applied Energy*, 331, 120444. <https://doi.org/10.1016/j.apenergy.2022.120444>
- [36] Wang, Y., Dai, Z., Chen, L., Shen, X., Chen, F., & Soltanian, M. R. (2023, February). An integrated multi-scale model for CO₂ transport and storage in shale reservoirs. *Applied Energy*, 331, 120444. <https://doi.org/10.1016/j.apenergy.2022.120444>
- [37] Yang, Y., Wang, K., Zhang, L., Sun, H., Zhang, K., & Ma, J. (2019). Pore-scale simulation of shale oil flow based on pore network model. *Fuel*, 251, 683–692.
<https://doi.org/10.1016/j.fuel.2019.03.083>

Vitae



Name :[Rajai A. Al Hubail]

Nationality :[Saudi]

Date of Birth :[8/3/1990]

Email :[Hubailra@gmail.com]

Address :[Saudi Aramco P.O. Box:- 12924, Dhahran 31311,
Eastern Province, Saudi Arabia]

[Mid-career Petroleum Systems analyst and renewable & low-carbon energy resources assessor, with a bachelor's degree in Geology. With around 13 years of experience that spans multiple roles in exploration such as Sequence Stratigraphy and Play-Based Exploration Concepts, Exploration Geochemistry, Basin Modeling, Charge System Analysis and Yet to Find Resource Assessment. Currently, in charge of Kingdom-wide regional studies related to Renewable and low-carbon energies' resource assessment. He is the project lead for play-based geothermal "stored-heat" resource assessment. His interests in geoscience include the integration of geochemistry, isotopes, and basin modeling. He has authored and co-authored multiple publications, including conference and workshop presentations and posters, on petroleum system-related topics. He is always passionate about pursuing higher degrees to advance career growth and personal development.]