

**NANOSCALE ASSESSMENT OF SHALES MECHANICAL
INTEGRITY UPON INTERACTIONS WITH
SUPERCRITICAL CO₂**

BY
DANDI ALVAYED

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This thesis, written by **Dandi Alvayed** 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 PETROLEUM ENGINEERING**.

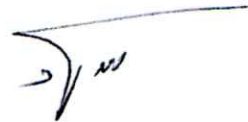


Dr. Dhafer Al Shehri
Department Chairman



Dr. Suliman Al-Homidan
Dean of Graduate Studies

May 14, 2024



19/05/2024

Dr. Saad Alafnaan
(Advisor)



22/05/2024

Dr. Murtada Aljawad
(Member)



27-05-2024

Dr. Abduljamiu Amao
(Member)

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[Dedicated to my lovely family]

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LIST OF ABBREVIATIONS

SEM : Scanning Electron Microscopy

TOC : Total Organic Carbon

XRD : X-ray diffraction

XRF : X-Ray Fluorescence

ABSTRACT

Full Name : Dandi Alvayed

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The increasing release of carbon dioxide (CO₂) into the atmosphere requires a thorough examination of methods to capture, use, and store CO₂ to mitigate the effects of global warming. To evaluate the feasibility of utilizing supercritical carbon dioxide (sc-CO₂) for waterless fracturing and CO₂ storage, it is crucial to understand the changes in geomechanical properties when shale interacts with sc-CO₂. The mechanical response of nanoscale constituents in shales remains inadequately understood due to the challenges associated with isolating them for comprehensive mechanical analysis without compromising their structural integrity. Nanoindentation is a valuable technique for exploring the heterogeneity of shale's mechanical properties in situ. This study presents a method for analyzing the mechanical variations in shale pre- and post-treatment with SC-CO₂. We combined nanoindentation with Scanning Electron Microscopy (SEM) to investigate these changes comprehensively. Mirror-like finished micro samples were extracted from a core plug and subjected to careful selection of fixed-force mode during excessive nanoindentation. Moreover, the mechanical assessment was complemented by Scanning Electron Microscopy (SEM) imaging to visualize morphological alterations. The samples were subjected to aging under sc-CO₂ conditions for 7, 30, and 60 days. The results reveal a dual peak distribution in the nanoscale measurements for the mechanical properties, indicating a comparable frequency of soft and hard constituents, validated by SEM mapping. Young's modulus and hardness values exhibit a wide range of mechanical heterogeneity at the nanoscale level, varying between 7 to 85 GPa and 0.3 to 4.9 GPa, respectively. Meanwhile, macroscale yield displays a normal distribution for Young's modulus values ranging from 25 to 60 GPa, representing the overall behavior of mechanical properties. Moreover, the results of CO₂ aging demonstrated a gradual weakening of the shale matrix with increasing sc-CO₂ exposure duration. This research introduces a novel framework for comprehensively investigating the mechanical properties of shales at both micro- and macroscale, complemented with high-resolution imaging. The findings shed light on the geomechanics of different shale constituents to provide a detailed understanding of the mechanical behavior at a larger scale.

ملخص الرسالة

الاسم الكامل: داندي الفايد

عنوان الرسالة: التقييم على نطاق النانو لسلامة الصخور الطينية عند تفاعلها مع ثاني أكسيد الكربون فائق الحرارة

التخصص: الهندسة البترولية

تاريخ الدرجة العلمية: مايو 2024

يتطلب التحرير المتزايد لثاني أكسيد الكربون في الغلاف الجوي إجراء فحص دقيق لطرق التقاط والاستخدام وتخزين ثاني أكسيد الكربون للتخفيف من آثار الاحتباس الحراري . لتقييم جدوى الاستفادة من ثاني أكسيد الكربون فوق الحرجة في التفتيت الخالي من الماء وتخزين ثاني أكسيد الكربون ، من الضروري فهم التغيرات في الخصائص الجيوميكانيكية عند تفاعل الصخور الطينية مع ثاني أكسيد الكربون . لا تزال الاستجابة الميكانيكية للمكونات في الصخور الطينية غير مفهومة بشكل كافٍ بسبب التحديات المرتبطة بعزلها للتحليل الميكانيكي الشامل دون المساس بالسلامة الهيكلية لها . يعد النانواندنيشن تقنية قيمة لاستكشاف تباين الخصائص الميكانيكية للصخور الطينية في الموقع . تقدم هذه الدراسة طريقة لتحليل الاختلافات الميكانيكية في الصخور الطينية قبل وبعد المعالجة باستخدام ثاني أكسيد الكربون . قمنا بدمج النانو اندنيشن مع المجهر الإلكتروني الماسح للتحقيق في هذه التغيرات بشكل شامل . تم استخراج عينات مجهرية مشطوفة كمرآة من سدادة أساسية وخضعت لاختبار دقيق لوضع القوة الثابتة . علاوة على ذلك ، تم استكمال التقييم الميكانيكي بالمجهر الإلكتروني الماسح لتوضيح التغيرات المورفولوجية . تعرضت العينات للتكسر تحت ظروف التفاعل مع ثاني أكسيد الكربون لمدة 7 و 30 و 60 يومًا . تكشف النتائج عن توزيع ذروة مزدوجة في القياسات النانوية للخصائص الميكانيكية ، مما يشير إلى تكرار مماثل للمكونات اللينة والصلبة ، وهو ما تم التحقق منه بواسطة رسم خرائط المسح المجهرية . تُظهر قيم معامل يونج والصلابة مجموعة واسعة من التباين الميكانيكي على مستوى النانو ، تتراوح بين 7 إلى 0.3 إلى 4.9 جيجا باسكال على التوالي . وفي الوقت نفسه ، يُظهر العائد على نطاق واسع توزيعًا طبيعيًا لقيم معامل 85 GPa جيجا باسكال ، مما يمثل السلوك العام للخصائص الميكانيكية . علاوة على ذلك ، أظهرت نتائج G يونج تتراوح بين 25 و 60 تفاعل ثاني أكسيد الكربون ضعفًا تدريجيًا لمصفوفة الصخور الطينية مع زيادة مدة التعرض لـ ثاني أكسيد الكربون . يقدم هذا البحث إطارًا جديدًا للتحقيق الشامل في الخصائص الميكانيكية للصخور الطينية على كل من المستوى المصغر والمستوى الكلي ، إلى جانب التصوير عالي الدقة . تلقي النتائج الضوء على الجيوميكانيكا لمكونات الصخور الطينية المختلفة لتوفير فهم تفصيلي . للسلوك الميكانيكي على نطاق أوسع .

CHAPTER 1

INTRODUCTION

1.1 Background

In recent years, the escalating exploration and extraction of unconventional resources, coupled with the growing concern over our planet's deteriorating climate, has sparked a profound emphasis on curbing carbon emissions and optimizing the utilization of carbon resources. This increased attention arises from the imperative to confront the environmental challenges that accompany such progress (Chen et al., 2018). At present, our world is confronted with a pressing need to investigate, with utmost care, methods that effectively capture, utilize, and store carbon dioxide (CO₂), given the exponential surge in atmospheric emissions of this greenhouse gas. These measures hold the key to mitigating the severe consequences of global warming that loom over humanity (Smith et al., 2016).

Supercritical carbon dioxide (sc-CO₂) has gained significant attention as an alternative fluid for hydraulic fracturing and CO₂ storage in shale formations (Bera et al., 2018). Understanding the modifications occurring in geomechanical properties when shale interacts with sc-CO₂ is crucial for assessing the viability of employing this technology. Given the influence of micro-scale mechanical properties on the overall mechanical behavior, it is essential to precisely determine and analyze the nano-scale properties of materials (Greer & De Hosson, 2011; Gao et al., 2003). The comprehension of the mechanical response exhibited by nanoscale constituents in shale formations is not well-understood as isolating them for thorough mechanical analysis while preserving their integrity is surrounded by high degree of uncertainty. Nanoindentation serves as a valuable

approach for in-situ exploration of the heterogeneity of shale's mechanical properties (Tang et al., 2016).

Geological units comprised of weak sedimentary rocks, such as clay shale and mudstone, are found in many places in the world. Construction failures of many large civil works and excavations in these weak rock masses have been encountered in North America and elsewhere. The objective of this research is to characterize Eagle Ford Shale at nanoscale level.

Shales, generally known as a type of fine-grained sedimentary rocks, are mainly composed of clay minerals and other secondary phases (e.g., quartz, calcite, and pyrite), as well as organic matter (e.g., kerogen). Owing to the wide size range of constituent particles (e.g., from $<2\ \mu\text{m}$ for clays to a few millimeters for sand particles) and different mineralogical compositions, shales are a class of complex, porous, multiphase, and multiscale composite materials. Microscopic observations via optical and electron microscopy or other imaging techniques show that fine-grained platy clay particles in shales exist in the form of highly compressed, preferentially oriented clay matrix that acts as the major load-supporting medium, while relatively coarse, anhedral, equidimensional silt and sand-sized particles are embedded as isolated solid inclusions within a mixed clay and organic matrix (the latter exists primarily in the voids of the clay matrix). Moreover, as a sedimentary rock, these constituent phases were initially highly compacted upon sedimentation and burial, followed by the formation of interparticle cementation via geological processes such as diagenesis, hydrothermal alterations, dissolution, and precipitation, among others, leading to the formation of rocks that exhibit both frictional and cohesive behavior. Therefore, the complex mechanical properties of shales are affected

by not only the mineralogical composition, particle size, and fraction of each constituent, but also the porosity and interparticle cementation.

Understanding the mechanical properties of bulk shale and its constituent phases is of vital importance for the geophysical subsurface exploration and subsequent long-term production of hydrocarbons from shale formations. Prior work studying the diverse aspects of mechanical properties of shales at multiple length scales show that it is very challenging to characterize and interpret the mechanical behavior of shales because of their heterogeneity and anisotropy (Johnston and Christensen, 1995). According to Smith et al. (2018), the assessment of micro-scale mechanical characteristics is crucial as they play a decisive role in shaping the overall mechanical response of materials. The micro-scale properties, such as hardness and modulus, directly influence the material's behavior at larger scales. Understanding and characterizing these micro-scale properties enable accurate predictions of macro-scale material behavior under different loading conditions (Jones & Johnson, 2019). According to Smith et al. (2020), the assessment of micro-scale mechanical properties is essential due to the significant impact of these properties on the material's overall mechanical behavior.

Nanoindentation is a technique used to interpret the mechanical properties of materials at the nanoscale level by indenting the surface of the material with a tip and evaluating the resulting deformation (Oliver & Pharr, 2004). It is particularly useful for characterizing thin films, coatings, nanoparticles, nanocomposites, and biological materials, where traditional macroscopic mechanical testing methods may not be applicable or accurate. This technique is widely used in materials science and engineering research to study the mechanical behavior of materials, including hardness, elastic

modulus, and toughness. The technique has numerous applications in areas such as materials design, biomaterials, and surface engineering (Fischer-Cripps, 2006). During a typical nanoindentation experiment, a controlled load is intentionally applied to the sample. This controlled load can be achieved by either specifying a particular force to be applied or defining the desired depth of penetration (Zeng et al., 2018). The selection of the load has to be made carefully to avoid misinterpretation of micro-scale mechanical properties as the tip might penetrate multiple layers (Brown et al. 2017).

To accurately determine the composition and morphology of shale samples, the SEM mapping technique can be employed, as highlighted by Johnson and Doe (2022). SEM mapping allows for the characterization of the elemental composition of shale and provides high-quality images that verify its morphology (Smith et al., 2021). This technique involves scanning the surface of the shale sample with a high-resolution electron beam, which interacts with the atoms in the sample, causing the emission of characteristic X-rays (Goldstein et al., 2018). The energy and intensity of these X-rays are then measured by the detector, allowing for the identification and quantification of the elements present in the shale (Heinrich & Newbury, 2012).

More recently, a grid or statistical indentation approach has been developed to probe the mechanical properties of highly heterogeneous, multiphase materials, particularly those consisting of a more homogeneous matrix with embedded granular solid inclusions, such as shales and concretes, via a massive number of measurements (Constantinides et al., 2006). Further statistical deconvolution of the voluminous experimental data yields insights into the mechanical behavior of individual constituent phases, but not the bulk rock whose properties are typically obtained by different

macroscopic testing. In addition, because different constituents in a shale usually have varied particle sizes, the maximum indentation depth selected for measuring the elasticity of individual constituents should not be fixed, but vary with different indent locations (e.g., based on the 10% rule of thumb, the maximum indentation depth should be limited to the 10% of the thickness or size of the tested material). The above statistical nanoindentation techniques bring an additional advantage for the study of composites such as shales. With the determination of the mechanical properties as well as fractions of individual constituent phases, the micromechanical models developed based on different homogenization and upscaling schemes can be used to estimate the pertinent macroscale properties of the bulk composites. In particular, the elastic modulus of a multiphase composite can be modeled by the Voigt and Reuss models for its upper and lower bounds, respectively (Hill, 1952; Reuss, 1929; Voigt, 1889).

This research presents a newly developed massive data-based nanoindentation approach for characterizing the mechanical properties of shales, a multiscale, multiphase composite material with solid inclusions. Combined with the newly formulated, rational data analytics as well as a surround effect model, the elasticity of both individual phases and the bulk rock crossing different length scales can be determined via a single type of mechanical testing (i.e., nanoindentation). In general, probing the elasticity of individual phases requires nanoscale measurements with infinitesimal indentation depths, while determination of the bulk rock's mechanical properties requires measurements at very large depths. This approach offers many advantages over other conventional measurement methods, one of which is obtaining the cross-scale mechanical properties via a single type

of mechanical testing. It can be expectedly implemented as an economical, effective, and efficient toolkit for cross-scale mechanical testing of rocks and other composite materials.

1.2 Knowledge Gap

1. How do mechanical properties and overall mechanical characteristics of shale at nanoscale change as a result of sc-CO₂ treatment?
2. How does sc-CO₂ long-term exposure impact the frackability of rock for hydraulic fracturing and CO₂ storage implications?

1.3 Objectives

1. Investigating the mechanical heterogeneity of organic-rich shale formations through integrating nanoindentation and Scanning Electron Microscopy (SEM), specifically focusing on analyzing the influence of long term sc-CO₂ treatment on the mechanical characteristics of shale.
2. Providing a macro to nanoscale mechanical properties crosslinking.
3. Conducting nanoscale mapping of the mechanical integrity of organic-rich shales upon exposure to sc-CO₂ utilizing nanoindentation techniques.

CHAPTER 2

LITERATURE REVIEW

The growing exploration and production of unconventional resources, coupled with the worsening state of global climate, has led to an amplified emphasis on the reduction of carbon emissions and the effective utilization of carbon resources. This heightened attention stems from the need to address the environmental challenges associated with these developments (Chen et al., 2018). There is an urgent need to carefully investigate methods for capturing, using, and storing carbon dioxide (CO₂) in light of the exponential increase in atmospheric CO₂ emissions. These measures are crucial to mitigating the severe consequences of global warming (Smith et al., 2016).

Supercritical carbon dioxide (SC-CO₂) has emerged as a potential anhydrous fracturing fluid for the development of unconventional reservoirs. This choice is driven by several advantages it offers, including the reduction of water consumption and the prevention of reservoir contamination (Smith et al., 2019). Supercritical carbon dioxide (SC-CO₂) is a fluid state of carbon dioxide above its critical temperature (31.1 °C) and critical pressure (7.38 MPa) (Hassanpouryouzband et al., 2019). In this state, CO₂ exhibits gas-like mass transfer properties and liquid-like density and solvency, making it a popular green solvent for various industrial processes such as extraction, separation, and cleaning (Lieberman et al., 2018). The unique properties of sc-CO₂ make it a promising alternative to traditional organic solvents due to its non-toxic, non-flammable, and non-corrosive nature, as well as its low environmental impact (Bruno et al., 2018).

In order to assess the viability of utilizing supercritical carbon dioxide (sc-CO₂) for waterless fracturing and carbon dioxide (CO₂) storage, it is imperative to acquire a

comprehensive understanding of the alterations in geomechanical properties that arise when shale is exposed to sc-CO₂ and to grasp the implications of the interaction between shale and sc-CO₂ (Cipolla et al., 2013; Osorno-Monsalve et al., 2018). This in-depth understanding plays a pivotal role in evaluating the potential of sc-CO₂ to enhance fracturing processes while minimizing water consumption and in determining its suitability as a medium for CO₂ storage (Ghanizadeh & Barati, 2020). By examining the geomechanical responses of shale to sc-CO₂ exposure, valuable insights can be obtained regarding the mechanical behavior and stability of the reservoir rock mechanical properties under such circumstance (Zhang et al., 2021; Elkatatny et al., 2018).

According to Smith et al. (2018), the assessment of micro-scale mechanical characteristics is crucial as they play a decisive role in shaping the overall mechanical response of materials. The micro-scale properties, such as hardness and modulus directly influence the material's behavior at larger scales. Understanding and characterizing these micro-scale properties enable accurate predictions of macro-scale material behavior under different loading conditions (Jones & Johnson, 2019). According to Smith et al. (2020), the assessment of micro-scale mechanical properties using nanoindentation on shale is essential due to the significant impact of these properties on the material's overall mechanical behavior.

Nanoindentation is a technique used to measure the mechanical properties of materials at the nanoscale level by indenting a small tip into the surface of the material and measuring the resulting deformation (Oliver & Pharr, 2004). This technique is widely used in materials science, engineering, and physics research to study the mechanical behavior of materials, including hardness, elastic modulus, and fracture toughness. The technique

has numerous applications in areas such as materials design, biomaterials, and surface engineering (Fischer-Cripps, 2006). Nanoindentation provides a valuable technique for characterizing shale's hardness, modulus, and other relevant properties at small length scales (Johnson & Doe, 2018). Nanoindentation is a commonly employed surface testing technique for evaluating the mechanical properties of materials.

In a typical nanoindentation experiment, the sample is subjected to a controlled load (either by applying a specified force or specifying the depth of penetration) and then unloaded (Zeng et al., 2018). The nanoindentation test allows for the examination of the influence of indentation parameters, such as the indentation force and contact depth, on the determination of micro-scale mechanical properties, as discussed by Brown et al. (2017). Nanoindentation permits for localized testing on shale samples, enabling researchers to gain insights into its mechanical response and improve their understanding of shale's structure-property relationships (Wang & Li, 2021). To accurately determine the composition and morphology of shale samples, the SEM mapping technique can be employed, as highlighted by Johnson and Doe (2022). SEM mapping allows for the characterization of the elemental composition of shale and provides high-quality images that verify its morphology (Smith et al., 2021).

When it comes to organic-rich shale, nanoindentation testing can offer valuable information about its mechanical properties, such as its hardness and modulus. This is important for various applications, including the extraction of oil and gas from shale formations, as well as for understanding the geomechanical behavior of shale formations during hydraulic fracturing. The polished surface of a shale sample is captured in **Figure 1** using a Scanning Electron Microscope (SEM) image, revealing the heterogeneous nature

of the sample (Ghassemi, Bobko, & Ma, 2014). The image showcases the presence of organic material, clay, and minerals such as pyrite and silicate within the shale sample. The combination of nanoindentation and SEM can measure the mechanical properties of materials including organic-rich sample at the nanoscale level and accurately determine the composition and morphology of shale samples (Oliver & Pharr., 2004).

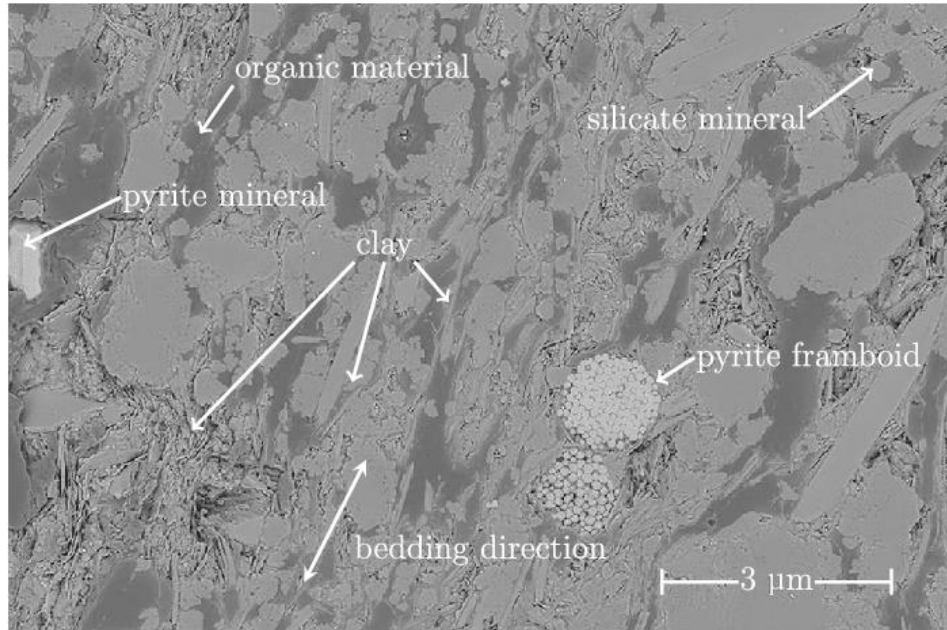


Figure 1. SEM image of polished shale sample surface (Ghassemi, Bobko, & Ma, 2014)

Organic-rich shale is a type of sedimentary rock that contains a high amount of organic matter, primarily composed of fossilized marine and terrestrial plants and animals (Zhang et al., 2019). These rocks are typically composed of fine-grained clay minerals and are known for their low permeability and high porosity, making them important sources of oil and natural gas through hydraulic fracturing (fracking) (Chalmers et al., 2012). Understanding its properties is essential for assessing the feasibility and productivity of shale gas and oil extraction operations (Wang et al., 2016). Organic-rich shale plays a vital role in the carbon cycle and climate change. It serves as a repository for organic carbon,

and the release of greenhouse gases during shale gas extraction can impact the environment (Huang et al., 2021).

The mechanical response of nanoscale constituents in shales remains inadequately understood due to the challenges associated with isolating them for comprehensive mechanical analysis without compromising their structural integrity. There has been a scarcity of research conducted to comprehensively investigate the mechanical properties of shale through nanoindentation techniques. Additionally, only a few studies have been conducted to examine the long-term impact of sc-CO₂ treatment on the mechanical characteristics of shale.

CHAPTER 3

METHODOLOGY

3.1 Sample Preparation

A series of experiments were performed in order to establish the feasibility of the CO₂ effect on shale samples. To enable clear visualization under a microscope, the organic-rich sample needs to be polished by two subsequent polishing procedures, which are mechanical and ion beam polishing procedures. For the mechanical polishing procedure on EM TXP (Leica), the large core kerogen-rich sample with a 1.5" diameter and a 4" length was chopped using Delta Petrocut into smaller pieces with a dimension of 1 mm in diameter and 0.5 mm in length, label by AI1, AI2, and AI3 respectively. The total organic carbon (TOC) content of the shale samples was determined using a dedicated TOC machine on the side core, yielding an approximate value of 2.7%. This result signifies that the samples contain a significant amount of organic material, indicating that they are organic-rich shale samples.

In order to facilitate the conduction of multiple nanoindentation tests, it was established as a prerequisite that the surface RMS roughness, as quantified by measurements taken with the Berkovich tip, must remain below the threshold of 100 nm over a defined area of 50 μm $\times$ 50 μm . To produce a mirror-like surface finish, the three selected samples were mechanically polished using 600 and 1200 grit silicon carbide paper by EM TXP (Leica) then will be successively finer diamond lapping foil starting at 9 micrometers (μm), 2 μm , and continuing until reaching 0.5 μm . Subsequently, the mirror-like surface sample will be transferred to the ion beam polishing on the EM TIC

3X (Leica) once the mechanical polishing process is finished in order to ensure a very flat surface and achieve a nanoscale of surface roughness. Prior to ion milling, the sample must be cleaned to get rid of any leftovers from the mechanical preparation. The cleaning stage of the ion beam EM TIC 3X uses the following parameters: incident angle of 15°, accelerating voltage of 5kV, duration of 15 min, medium rotation, and lateral movement of +/-5 mm. The samples will next be polished with an ion beam under the following conditions: incident angle of 4.5°, accelerating voltage of 6kV, total time of 120 min, medium rotation, and lateral movement of +/-5 mm. Additionally, in order to prevent organic material evaporation, the sample will be milled for 10 min and subsequently cooled for 10 min. This process will be repeated until the total time reaches 120 min. With the use of the Zeiss Gemini 550 FIBSEM procedure, the polished samples were finally imaged and marked with a very high-resolution image (micro to nanoscale) via scanning electron microscope (SEM) for noting the coordinates of the grid position. The samples were then transferred to the Hysitron TI 980 nanoindenter (Hysitron, Inc., Minneapolis, MN) to obtain mechanical properties of the rock. **Figure 2** depicts the experimental setup utilized in this study. The apparatus (a) Delta Petrocut, (b) Leica EM TXP, (c) Leica EM TIC 3X, (d) Hysitron Nanoindenter TI980, and (e) Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM-EDX) include several key components that play crucial roles in conducting the experiment.

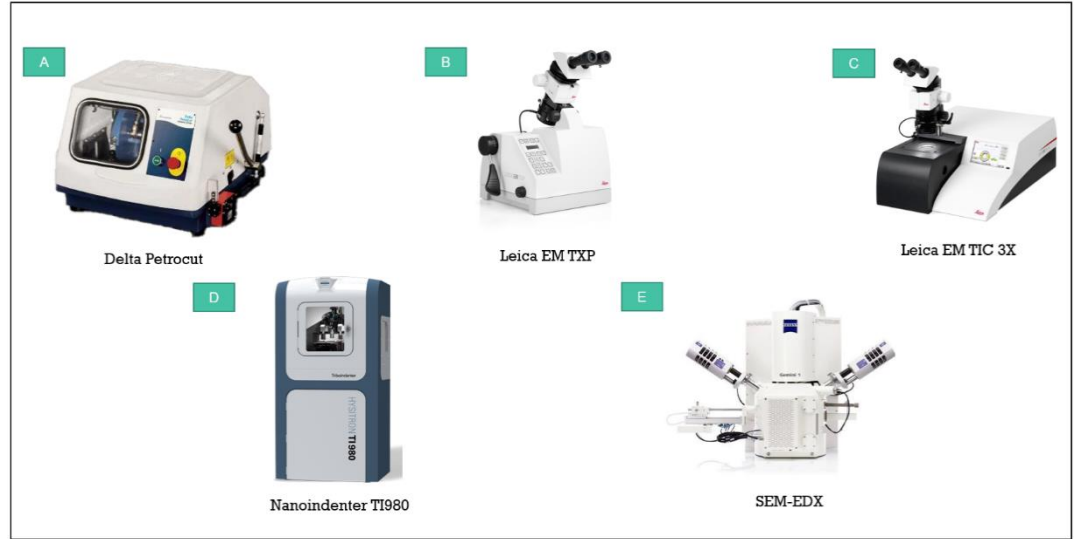


Figure 2. The apparatus used in this experiment a) Delta Petrocut, (b) Leica EM TXP, (c) Leica EM TIC 3X, (d) Hysitron Nanoindenter TI980, and (e) Scanning Electron Microscope

3.2 Nanoindentation Design for sc-CO₂ Treatment

The experimental design for studying the interactions between shale and sc-CO₂ involved conducting nanoindentation tests and analyzing the effects of sc-CO₂ treatment on the shale samples. Schematic diagrams were utilized to illustrate the key components and processes of the experimental setup, as illustrate by **Figure 3**. Experiments were conducted using a nanoindenter called Hysitron TI 980, which is capable of continuously monitoring loads and displacements. This instrument allows for the direct calculation of material hardness and elastic modulus without the need to image the indentation imprint. The tests were performed at room temperature on the central area of the sample using rectangular arrays consisting of a 20 x 20 grid with 20 μm spacing on the polished surfaces. The nanoindenter used in the experiments had a displacement resolution of 0.01 nanometers, meaning it could accurately measure displacements as small as 0.01 nm.

Similarly, the load resolution was 100 nanoNewtons, allowing for precise load measurements at increments of 100 nN. In the tests, a fixed load of 10,000 microNewtons (μN) was applied throughout, and the humidity level was not controlled.

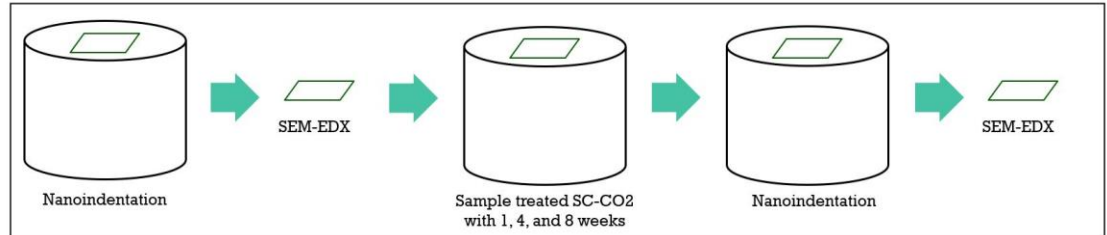


Figure 3. Illustrations demonstrating the experimental design for studying interactions between shale and supercritical carbon dioxide (SC-CO₂).

During the experiments, the loading rate was set at 200 $\mu\text{N/s}$, meaning the load applied to the sample increased at a constant rate of 200 microNewtons per second. Data acquisition occurred at a rate of 200 points per second, allowing for detailed measurements and capturing the behavior of the material during the indentation process. The depth of penetration for individual indentations varied, ranging from approximately 0.5 micrometers to 12 micrometers. This range indicates the extent to which the indenter pressed into the material, providing insights into its mechanical properties and response to external forces.

Before and after treating the samples with sc-CO₂ (supercritical carbon dioxide) fluid, each sample underwent 400 indentations using a Berkovich pyramidal indenter. sc-CO₂ is a state of carbon dioxide that occurs above its critical temperature of 31.1°C and critical pressure of 7.38 MPa, while at lower temperatures it exists as a liquid. To mimic the pressure and temperature conditions of a reservoir environment, the pressure and

temperature were set to 13.79 MPa (2000 Psi) and 75°C, respectively, for durations of one week, one month, and two months.

To ensure accuracy, the indenter was calibrated before each test using both quasi and air indentation methods. This calibration process helped establish the proper settings and parameters for the experiments. After completing the indentation tests, the remaining indentation marks were used as reference points to locate the specific indentation array under the scanning electron microscope (SEM) for further analysis. Overall, the experiments involved using a nanoindenter to perform multiple indentations on the samples with precise monitoring of loads and displacements. The samples were treated with sc-CO₂ fluid, and the effects of this treatment were evaluated by comparing the indentation results before and after the treatment. The sc-CO₂ treatment aimed to replicate the pressure and temperature conditions found in reservoirs. The aim was to understand the interactions between shale and sc-CO₂ and evaluate any changes in material properties resulting from the treatment.

CHAPTER 4 | INTEGRATIVE ANALYSIS OF MECHANICAL HETEROGENEITY IN ORGANIC-RICH SHALES: BRIDGING NANO- AND MACROSCALE PROPERTIES FOR AN ENHANCED GEOMECHANICAL UNDERSTANDING¹ |

Abstract - The investigation of shale's mechanical properties, driven by its crucial role in hydraulic fracturing and rock physics modeling, has been a prominent focus in the past decade. The heterogeneous structure of shale matrix presents a challenge in characterizing and interpreting their mechanical behavior, necessitating a detailed understanding of their mechanical properties at various scales. Since micro-scale mechanical properties govern overall behavior, precise determination and analysis of the properties at the nanoscale become imperative. However, the complexity of nanoscale behavior, lack of standardized testing protocols, and limited cross-scale characterization and integration techniques for comprehensive mechanical analysis of shale heterogeneity led to a high degree of uncertainty in modelling shales geomechanics. This study introduces a method for investigating the mechanical heterogeneity of samples from Eagle Ford shales through a combination of nano-indentation and macroscopic mechanical testing. The results reveal a dual peak distribution in the nanoscale measurements for Young's modulus and hardness properties, indicating a comparable frequency of soft and hard constituents, validated by SEM mapping. Young's modulus and hardness values exhibit a wide range of mechanical

¹ This chapter replicates the content of the author's manuscript submitted to the Journal of Geomechanics for Energy and the Environment

heterogeneity at the nanoscale level, varying between 7 to 85 GPa and 0.3 to 4.9 GPa, respectively. Meanwhile, macroscale yield displays a normal distribution for Young's modulus values ranging from 25 to 60 GPa, representing the overall behavior of mechanical properties. The properties at different locations within the core plug at the nanoscale were statistically correlated with macroscopic properties. The study revealed that the macroscopic behavior is influenced by both soft and hard components in a proportionality corresponding to their frequencies. The reported outcomes offer valuable input for improved modeling and designing of stimulation processes to exploit shale resources further.

Keywords: Shale characterization, Multiscale analysis, Mechanical properties, Nano-indentation, Geomechanics

4.1 Introduction

In recent years, the extraction of crude oil and natural gas from unconventional shale formations has emerged as a pivotal source of hydrocarbon energy, primarily due to the economic viability enabled by production stimulation techniques (Jin et al., 2017; Rao, 2012; Xiong et al., 2017). Precise modelling of hydraulic fracturing extent and propagation rely on accurate determinations of the mechanical properties of shale reservoirs. The process is designed to create expansive networks (Lu et al., 2019). Intuitively, the successful execution and the integrity post-stimulation are controlled by the mechanical properties of the rock matrix (Chatterjee & Pal, 2010; Yasui et al., 2017; Zeng et al., 2018). Therefore, a rigorous understanding of the shale's mechanical properties holds the potential to enhance the planning and execution of hydraulic fracturing operations.

As fine-grained sedimentary rocks, shales comprise clay minerals, secondary phases like quartz and calcite, and organic matter such as kerogen, forming a multiphase composite (Kanitpanyacharoen et al., 2012; Zou et al., 2010). Microstructural examinations reveal the presence of densely compacted, ultra-low permeability clay particles conferring complex frictional and cohesive geomechanical properties (Luo et al., 2020; Seiphoori et al., 2017). Logically, macroscale attributes derive from individual constituents. Thus, accurately determining nanoscale mechanical characteristics is important (Locock et al., 2012).

Investigating the mechanical properties across various length scales has highlighted considerable challenges in characterizing and interpreting shales geomechanics, primarily due to their inherent heterogeneity and anisotropic nature (Josh et al., 2012; Sone & Zoback, 2013). Conventional methodologies (e.g., triaxial testing, uniaxial compression), originally devised for macroscopic testing, possess the capability to determine the mechanical attributes of the overall rock as a composite entity (He et al., 2022; Hsu & Nelson, 2002; Villamor Lora et al., 2016). However, these methodologies exhibit deficiencies in their ability to interrogate the mechanical characteristics of minute individual constituents, as they exclusively yield averaged bulk properties. This leads to a high degree of uncertainty when data are extrapolated in formations of different composition. Prior studies have documented inconsistent outcomes of the mechanical properties of shale in various locations (refer to **Table 1**), attributed to inherent variability in mineral behavior within distinct rock formations or even similar rocks with differing geological contexts (Fan et al., 2019; Rybacki et al., 2015; Yan et al., 2023). Consequently,

a significant knowledge gap persists in correlating the macroscopic mechanical characteristics to the constituents of the rock.

In the last two decades, nano-indentation has been widely used to study the mechanical properties of various materials at the nano to microscale (Oliver & Pharr, 1992, 2004). Recent developments have expanded the scope of nano-indentation with Scanning Electron Microscope (SEM) to encompass complex mineralogy composites, including shales and other rocks (Bennett et al., 2015; Bobko & Ulm, 2008; Hou et al., 2016; Veytskin et al., 2017; Yang et al., 2018). The introduction of a grid indentation technique has shown promise in offering valuable insights into the mechanical properties of discrete mineralogy within composite materials like shales, even for small-scale specimens with constrained dimensions (Constantinides et al., 2006). Prior investigations have primarily focused on specific areas of interest of a few microns, providing great insights into the variation of mechanical properties. However, the upscaling of the observed nanoscale behavior to the macroscale has yet to be bridged, as the range of properties changes significantly depending on location. Hence, developing an innovative nano-indentation protocol that is statistically representative holds substantial practical significance to explaining and modelling the core-scale mechanical behavior. This paper establishes a framework to delineate the mechanical properties of shales at the nano to macroscale level, complemented by high-resolution imaging through combining nano-indentation mapping and scanning electron microscopy analysis with macroscopic testing methods.

Table 1. Literature-reported Young's modulus (E) and TOC of some shales (Yan et al., 2023)

Sample	TOC/vol%	E/GPa
Eagle Ford1	14.3	12.2
Eagle Ford2	13.2	22.32
Marcellus1	1.2	48.69
Marcellus2	1.7	24.08
Alum	16.5	16.7
Barnett	13.8	46.4
Dotternhausen	14.9	8
Wickensen1	17	8
Wickensen2	18.3	7.2
Harderode	10.5	14.1
Haddessen	10.8	11.6

4.2 Methodology

4.2.1 Workflow

Figure 4 provides an overview of the workflow designed to comprehensively assess the mechanical properties of shale at the nano and macroscale. The process begins with the initial step of sample preparation, a critical first step for subsequent analysis at

both levels. Macroscale measurement starts by testing surface roughness before conducting mechanical properties assessment. The shale specimen undergoes various procedures for nanoscale phase preparation, including precise cutting and surface polishing, ensuring that the rock meets the specifications for further investigation. Additionally, thorough cleaning process removes potential contaminants, and high-resolution imaging techniques are used to confirm the specimen's suitability for in-depth analysis. Following the sample preparation, the workflow progresses into mineralogical and elemental determination experiments, which are important in acquiring a comprehensive evaluation of the shale's chemical composition and properties. The shale sample undergoes mechanical testing at both nano and macro scales to thoroughly characterize its mechanical response. The workflow is concluded with a systematic statistical analysis of the data collected throughout the preceding stages. This final phase serves to consolidate the acquired information and transforming it into quantitative insights.

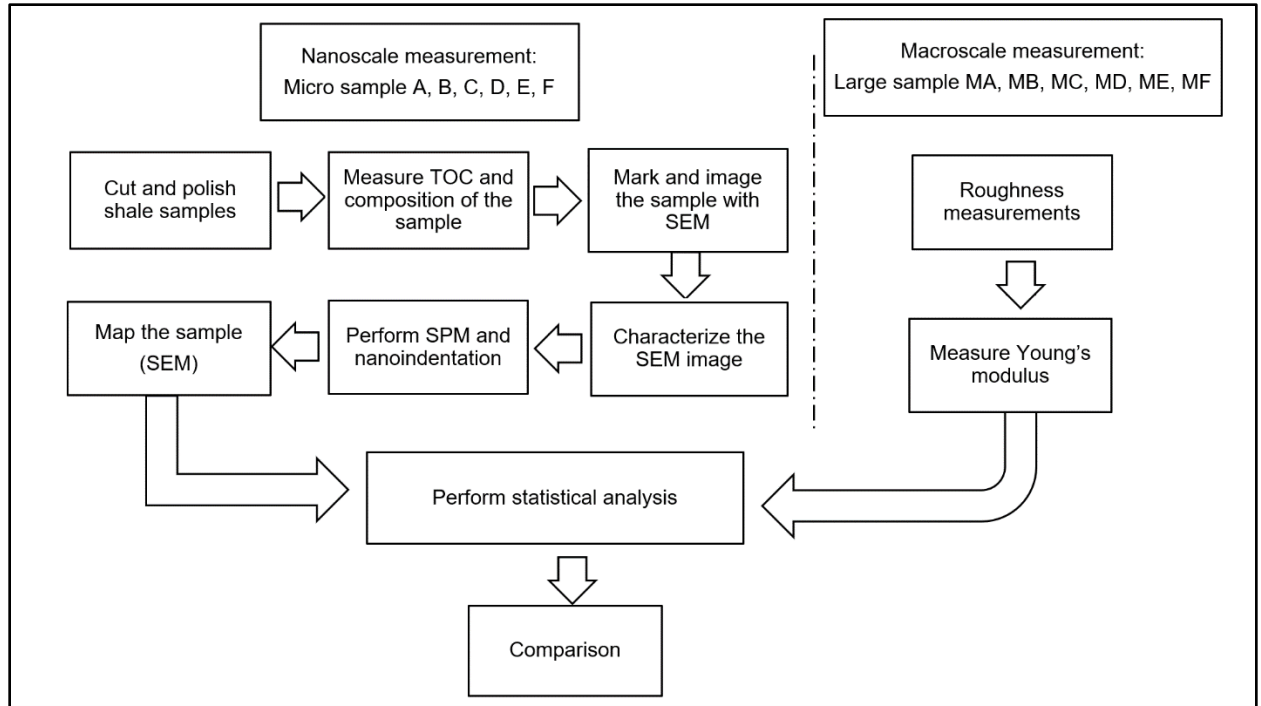


Figure 4. Workflow designed to comprehensively assess the mechanical properties of shale from nano to macroscale

4.2.2 Sample Preparation

Six Eagle Ford shale core samples were obtained for the study and utilized for the macro and nanoscale mechanical testing, as detailed in this subsection. **Figure 5** displays the prepared samples for (a) nanoscale and (b) macroscale experiments. It is important to highlight that the micro samples were cut from the same set of macro-ones to assure consistency and representative collection of data. The micro samples of shale underwent a two-step polishing process, comprising mechanical and ion beam procedures, to reduce surface roughness in preparation for nano-indentation testing and to facilitate clear visualization under SEM. During the mechanical polishing stage, the cylindrical specimens, initially measuring 1.5 inches in diameter and 3 inches in length, were sectioned into smaller pieces, each measuring 1 cm in diameter and 0.5 cm in length, using Delta

Petrocut and EM TXP (Leica) equipment. To produce a mirror-like surface finish, the six selected micro-samples underwent a sequence of mechanical polishing steps, beginning with 600 and 1200 grit silicon carbide paper, followed by successive stages of finer diamond lapping foil, beginning at 9 μm and progressing to 2 μm , ultimately reaching 0.5 μm . Before the ion milling treatment, ensure a thorough cleansing of the sample to eliminate any residues stemming from the preceding mechanical preparation. The cleaning procedure utilizing the ion beam EM TIC 3X (Leica) entails specific parameters, including

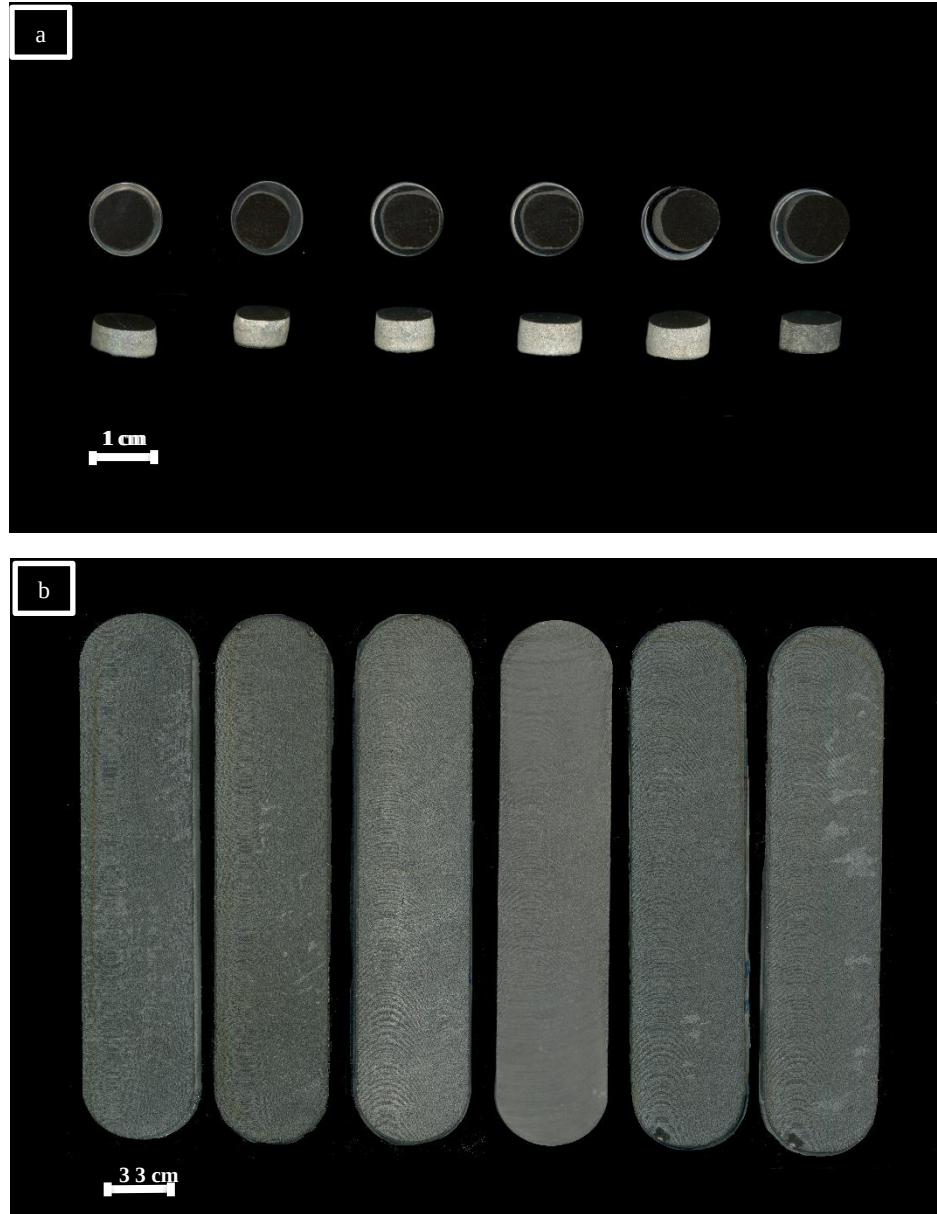


Figure 5. Samples prepared for (a) nanoscale and (b) macroscale experiments.

an incident angle set at 15° , an accelerating voltage of 5kV, a duration of 15 minutes, medium rotation, and lateral movement within a range of ± 5 mm. Subsequently, the specimens underwent ion beam polishing under the following conditions: an incident angle of 4.5° , an accelerating voltage of 6kV, a total processing time of 120 minutes, medium rotation, and lateral movement within a range of ± 5 mm. Furthermore, to mitigate the effects of sample evaporation, a milling duration of 10 minutes was followed by a cooling

period of 10 minutes, and this cycle will be iteratively repeated until the cumulative milling time reaches 120 minutes. Subsequently, utilizing the Zeiss Gemini 550 Focused Ion Beam Scanning Electron Microscopes (FIBSEM) procedure, the polished samples were subjected to high-resolution imaging at the micro to nanoscale using SEM. This imaging step established and recorded the precise coordinates of the grid positions. Subsequently, the specimens were transferred to the Hysitron TI 980 nanoindenter system to perform the mechanical characterization.

4.2.3 X-ray Diffraction, X-Ray Fluorescence and rock evaluation experiments

The mineralogical and elemental composition of the samples were obtained by incorporating both X-ray diffraction (XRD) and X-Ray Fluorescence (XRF) techniques (Amao et al., 2022). XRD analysis of the prepared samples was done by a Panalytical Empyrean (Under 45kV/40mA - X-Ray, 2 θ / θ -Scanning mode). Additionally, XRF was conducted utilizing M4 TORNADO (μ -XRF: Bruker Nano GmbH) equipped with a micro-focused rhodium source, which operates at 50 kV and 600 μ A, and a polycapillary optic ($\sim$ 20- μ m spot-size). Furthermore, Total Organic Content (TOC) was assessed using the Rock-Eval 6 setup (Carvajal-Ortiz & Gentzis, 2015). This instrument is widely recognized for its capability to provide precise measurements of organic carbon content, offering valuable insights into the composition of the materials. In the preparation for these analyses, small rock chips were crushed, resulting in particle sizes of less than 4 μ m (Locock et al., 2012). These combined analytical methods provided comprehensive insights into the shale sample's mineralogical content and elemental ratios.

4.2.4 Nanoscale experiments

The methodology and operational principles of the nano-indentation technique have been thoroughly documented and elucidated in previous publications (Fischer-Cripps & Nicholson, 2004; Oliver & Pharr, 1992). A typical result of the nano-indentation testing procedure yields an indentation load-depth hysteresis curve, as illustrated in **Figure 6**. Nano-indentation entails the establishment of contact between a specimen and an indenter tip characterized by precisely defined geometry and mechanical properties. Subsequently, a continuous load is applied while simultaneously measuring the corresponding indentation depth. Measuring the indenter's displacement post-contact with the sample and knowing the shape of the indenter allows for calculating the indentation area. Subsequently, indentation hardness can be determined by dividing the peak load (P) by the area of indentation (A) at that peak load as shown in Eq. (2.1). Furthermore, a reduced Young's modulus (E_r) indicates that displacements occur in both the sample and the indenter, and it is calculated using Eq. (2.2) where S is Stiffness. Finally, Young's modulus of the sample is determined by dividing uniaxial stress by uniaxial strain. This calculation is based on the expression provided in Eq. (2.3) where ν and ν_i represent the Poisson ratio of the sample and the diamond tip, respectively, while E_i stands for the Young's modulus of the diamond tip. In this experiment, tests were conducted utilizing a Hysitron TI 980 nanoindenter (Hysitron, Inc., Minneapolis, MN) to obtain Young's modulus and hardness of the sample.

$$H = \frac{P}{A} \quad (2.1)$$

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A}} \times S \quad (2.2)$$

$$E = \frac{1 - \nu^2}{\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}} \quad (2.3)$$

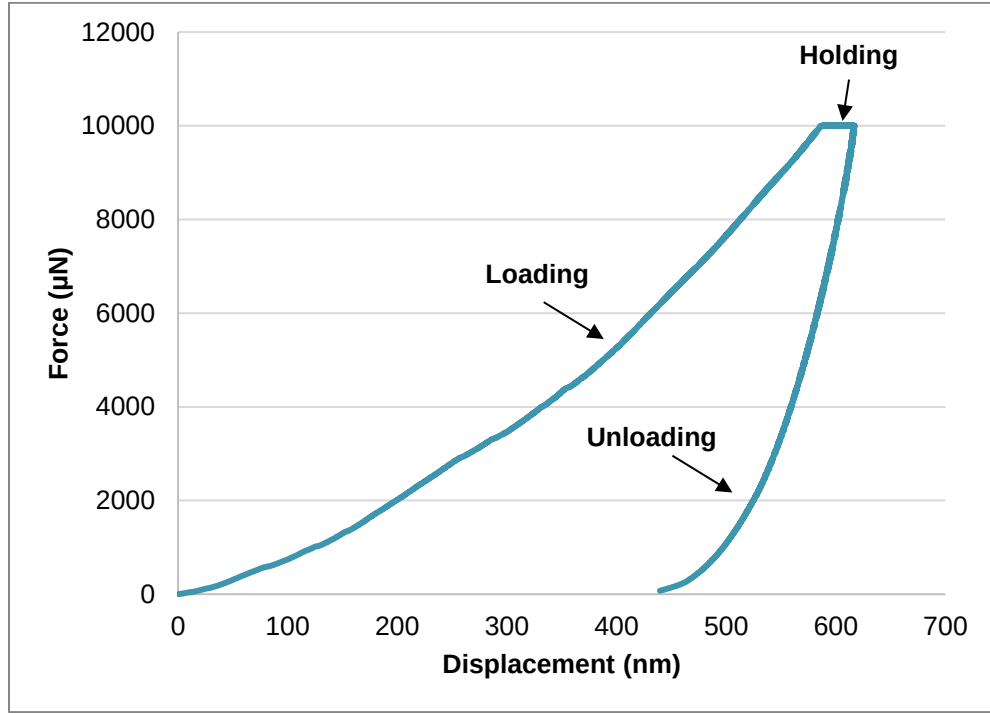


Figure 6. A representative outcome of the nano-indentation testing procedure, demonstrating an indentation load-depth hysteresis curve.

Surface roughness have the potential to introduce inaccuracies in indentation measurements. Consequently, ensuring the adequacy of surface smoothness is imperative for the precision of the indentation measurements (Du et al., 2018; Lucas et al., 1998). The surface roughness of the rock specimens was assessed by the TriboScanner Tandem Tube piezo scanner integrated within the TI 980 TriboIndenter system. This instrument facilitates in-situ scanning probe microscopy (SPM) for evaluating the substrates' surface topography before the indentation procedure's commencement.

Previous studies applied the concept of grid indentation to interpret indentation results in terms of the mechanical properties of the diverse microstructure at specific locations (Constantinides et al., 2003, 2006; Constantinides & Ulm, 2007). In this experiment, rectangular arrays of nano-indentations were systematically created on the polished sample surfaces using a standard Berkovich diamond probe with Young's modulus of 1140 GPa and Poisson's ratio of 0.07. These indentations were performed at ambient room temperature. Each region of the sample was subjected to an array consisting of 20×20 indentations (400 individual indentations), spaced at 10,000 nm intervals, with an applied load of 10,000 μ N. The maximum depth of penetration for unique indentations ranged from approximately 500 to 1500 μ m. Moreover, the nano-indentation imprints provided a reference for locating the indentation array under the optical microscope following the indentation experiments. Each micro sample underwent a repetition of measurements three times in random locations, resulting in a cumulative total of 1,200 individual indentations for a single sample. The target was to encompass the surface heterogeneity by randomly landing on different spots. Across all six samples with 18 different locations, this approach generated a dataset of 7,200 individual indentations, which by far exceeds the frequency of surface mapping in prior studies (Liu et al., 2018; Shi et al., 2020; Wang et al., 2022). This rigorous repetition of measurements was employed to enhance the statistical robustness and reliability of the acquired data, ensuring a comprehensive assessment of the mechanical properties of the specimens under investigation. Thereafter, the specimens were transferred to the SEM (Zeiss Crossbeam 550) to conduct a visual analysis of the surface characteristics depicted in the residual indent images.

4.2.5 *Macroscale experiments*

The AutoScan® instrumentation, developed by New England Research, Inc. (NER Inc.), was employed to assess the macroscale mechanical properties of the six macro samples, employing a range of interchangeable probes. A prop affixed to the scanner head was precisely positioned at designated locations within each sample, applying a predetermined force. The six large specimens, each measuring 6 x 1.5 x 0.5 inches, facilitated the acquisition of Young's modulus data at 30 distinct points on the surface for each individual sample, amounting to a total of 180 data points across all six samples. Additionally, laser scanning profilometry (Kruss surface roughness analyzer-SRA) was applied to assess the surface roughness of the samples. This analysis is crucial for understanding the microtopography of the shale sample, contributing to a more comprehensive characterization of its physical properties. The utilization of advanced techniques, such as laser scanning profilometry, enhances the precision and reliability of the surface roughness assessment, providing valuable data for further interpretation and correlation with other mechanical properties.

4.3 Results and discussions

4.3.1 *Shale material*

X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses are pivotal techniques employed for the elemental and mineralogical characterization of geological samples, particularly shale (Amao et al., 2022; Hazra et al., 2016). In our current study, the analyzed samples revealed a predominant mineral distribution comprising, 40.5% Pyrite,

15.2% Dickite, 14.3% Muscovite, 11.8% Quartz, and 11% Kaolinite, with primary elemental components identified as Fe, Si, S, and Al, as illustrated in **Figure 7a,b**.

The significant abundance of Pyrite at 40.5% underscores its prominence in the shale's mineral makeup. Quartz, constituting 11.8% of the samples, is recognized for its robustness against weathering processes, as indicated by a previous study (Heyliger et al., 2003). The presence of 15.2% Dickite contributes to the shale's properties by influencing factors such as plasticity and porosity and 11% Kaolinite suggests extensive weathering of feldspar minerals within the sample as per previous studies (Buntoro et al., 2022; Sato et al., 2005).

The samples have an average Total Organic Carbon (TOC) content of 2.7 wt%, indicating the substantial presence of organic material and generally considered indicative of organic-rich shale (Speijer & Wagner, 2002). Hence, the samples offer an opportunity to explore the role of organic matter in the mechanical behavior of shales.

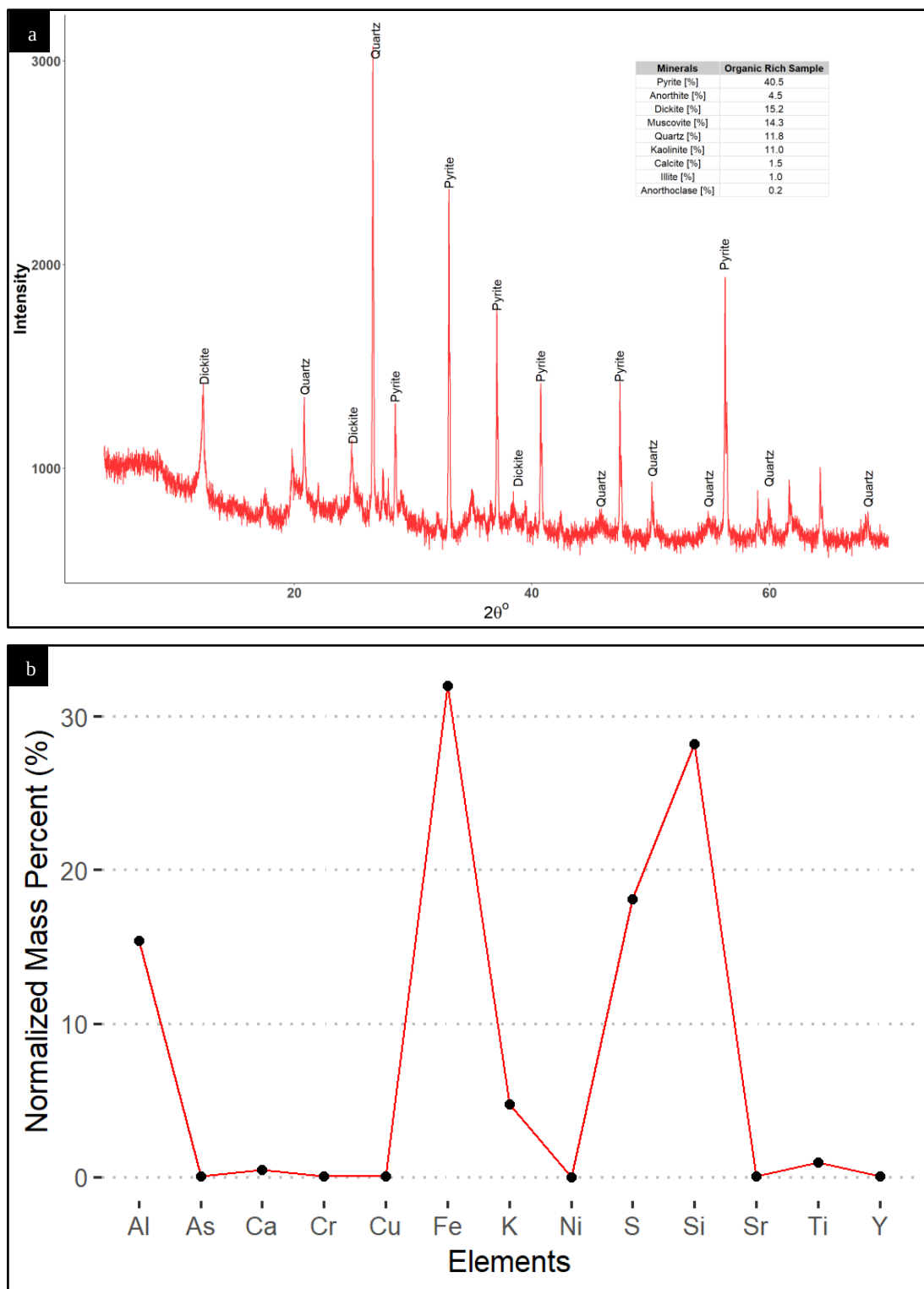


Figure 7. Result of (a) XRD and (b) XRF tests.

4.3.2 Nanoscale mechanical properties

Surface roughness is widely regarded as a potential source of inaccuracies in indentation measurements, representing a key factor contributing to discrete indentation data (Xie & Tang, 2022). Error! Reference source not found. **Figure 8** depicts the topography of shale samples, specifically for samples C and D as examples. The Root Mean Square (RMS) roughness was determined to be 69.1 nm for sample C and 50.3 nm for sample D. These values align with the criteria established in a previous study (Wang et al., 2022), indicating that the samples are deemed suitable for subsequent nano-indentation testing.

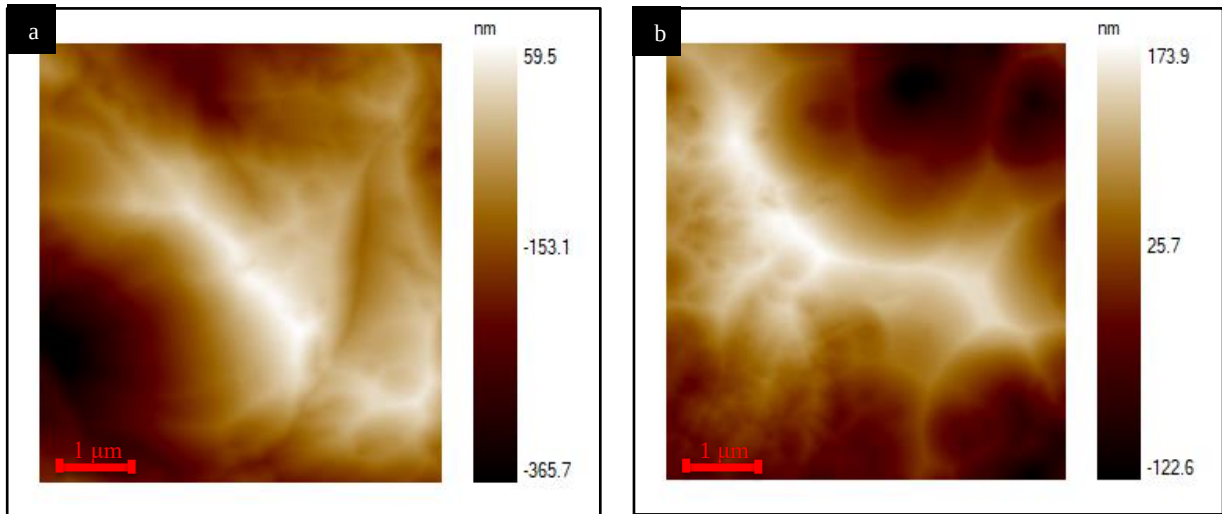


Figure 8. SPM topography of shale rock surfaces (a) Sample C and (b) Sample D

Table 2 provides an overview of the mechanical properties, specifically Young's modulus and hardness, across all six micro samples. Young's modulus (E) values for the samples ranged from 37.13 to 52.56 GPa, with Sample A exhibiting the maximum value while Samples E and F showed the minimum values. This indicates variation in the

mechanical properties across the different micro samples. The values of hardness ranged from 1.67 to 2.46 GPa, with Sample A exhibiting the maximum hardness while Samples E and F showed the minimum hardness. Higher hardness values suggest a more rigid material, while lower values indicate a relatively softer material (Musil et al., 2002). Samples E and F exhibit higher standard deviations, indicating increased variability in their measurements compared to the other samples (Altman & Bland, 2005). The latter provides a better understanding of the precision of the mean estimate. For instance, Sample A has a mean E of 52.56 GPa with an standard deviation of 2.46 GPa, and a 95% confidence interval for E of (51.91 GPa, 53.21 GPa).

Table 2. Statistical analysis of the mechanical properties of six samples (A, B, C, D, E, and F) with respect to Young's Modulus (E) and hardness (H)

Sample ID	Frequency	Mean		Standard Deviation		95% Confidence Interval	
		E	H	E	H	E	H
		(GPa)	(GPa)	(GPa)	(GPa)	(GPa)	(GPa)
Sample A	1200	52.56	2.46	12.61	0.75	(51.91, 53.21)	(2.41, 2.50)
Sample B	1200	45.73	2.27	10.75	0.75	(45.08, 46.38)	(2.22, 2.32)
Sample C	1200	46.67	2.14	11.89	0.86	(46.02, 47.32)	(2.09, 2.19)
Sample D	1200	40.42	2.16	11.12	0.76	(39.78, 41.07)	(2.11, 2.21)
Sample E	1200	37.13	1.67	10.02	0.88	(36.48, 37.78)	(1.62, 1.72)
Sample F	1200	37.47	1.73	11.98	1.06	(36.82, 38.11)	(1.68, 1.78)

In **Figure 9**, the observed distribution exhibits a discernible dual peak pattern. Specifically, in Region C1, C2, and C3, the mean values of Young's modulus are reported as 46.69 GPa, 45.53 GPa, and 47.59 GPa, respectively, resulting in an overall mean Young's modulus for Sample C of 46.67 GPa. Correspondingly, the mean values of hardness in these regions are 2.08 GPa, 2.03 GPa, and 2.31 GPa, with an aggregate mean hardness for Sample C calculated as 2.14 GPa (as depicted in **Figure 9a,c**). Furthermore, it is noteworthy that all three locations within Sample C consistently manifest a dual peak pattern distribution in both Young's modulus and hardness, as visually represented in **Figure 9b,d**. The term "dual peak pattern" denotes the presence of two prominent peaks or high-frequency regions in the nanoscale distribution of Young's modulus and hardness in Sample C. This observed bimodal distribution is indicative of a distinct mechanical heterogeneity within Sample C at the nanoscale, wherein two prevalent constituents of the material are consistently identified across multiple locations.

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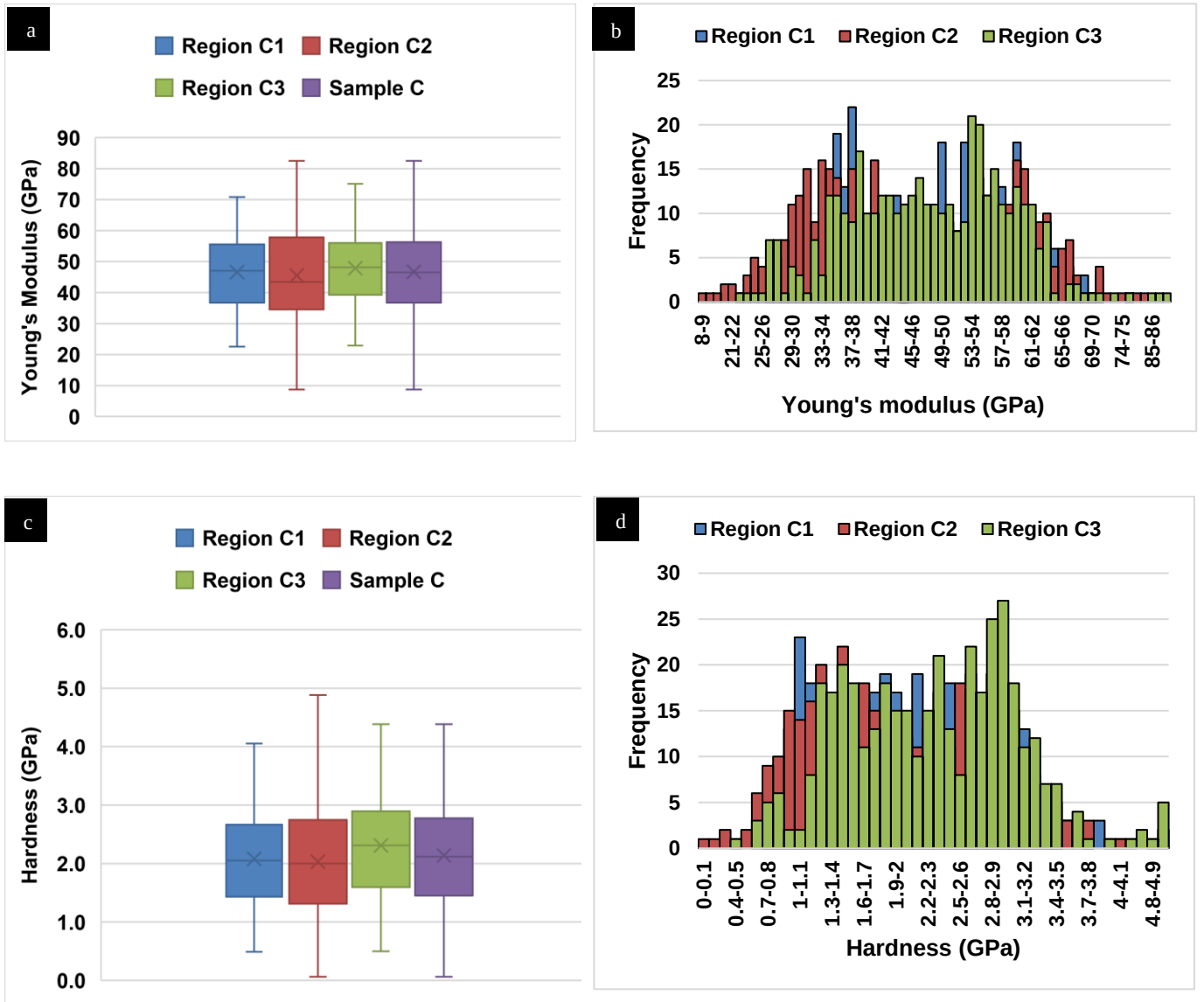


Figure 9. Nanoscale (a) Young's modulus values, (b) Young's modulus distribution, (c) hardness values, and (d) hardness distribution for Sample C

In contrast, Sample D exhibited varied behaviors in three different locations. Despite regional differences, an overall dual peak pattern was consistently observed across the entire sample. **Figure 10** delineates the nanoscale distribution of Young's modulus and hardness properties within Sample D, highlighting variations in behavior among the

different locations. The mean values of Young's modulus for regions D1, D2, and D3 were reported as 48.16 GPa, 41.48 GPa, and 31.63 GPa, respectively, resulting in an overall mean Young's modulus for Sample D of

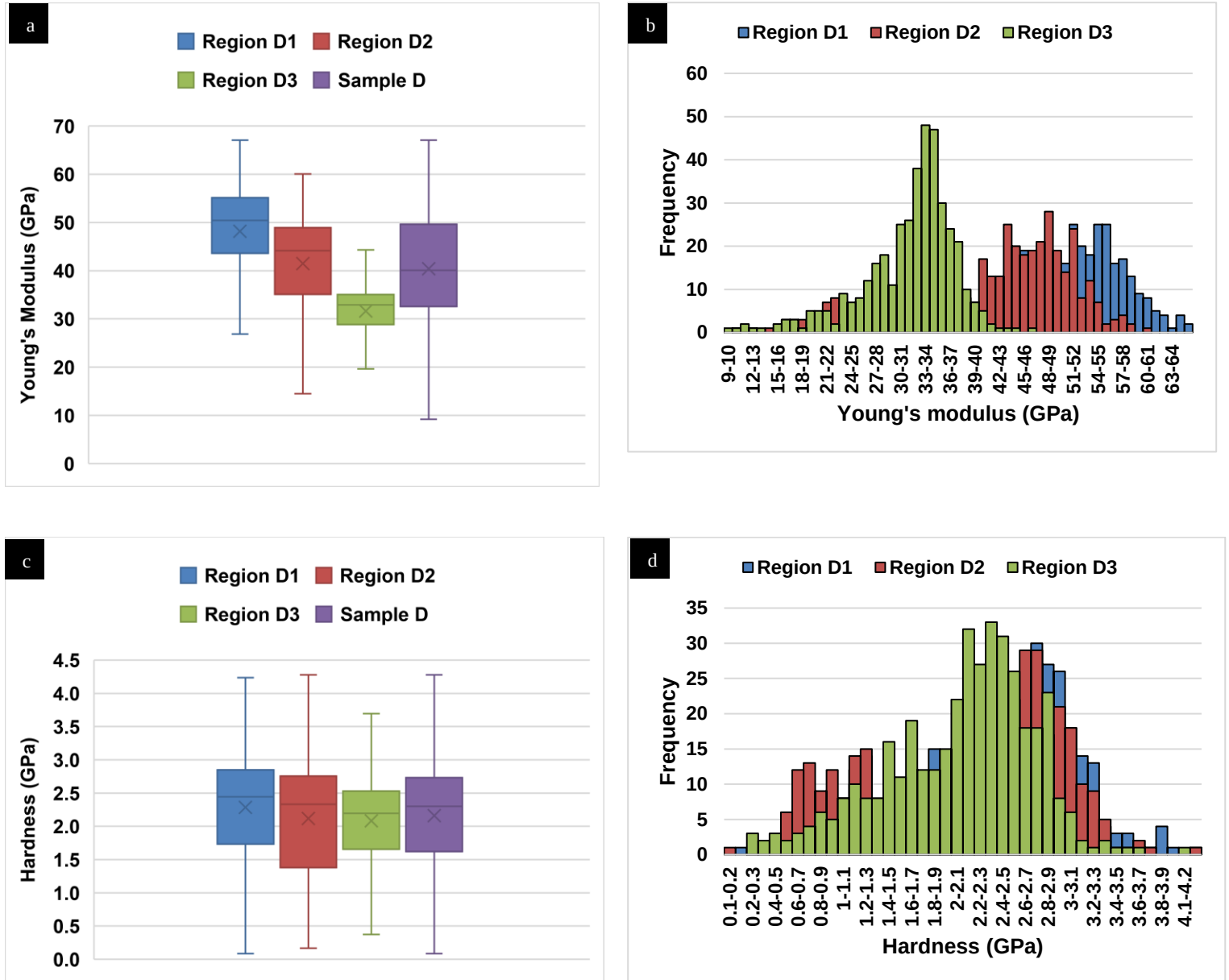


Figure 10. Nanoscale (a) Young's modulus values, (b) dual peak pattern distribution of Young's modulus, (c) hardness values, and (d) dual peak pattern distribution of hardness for Sample D with different behavior from three different locations

40.42 GPa. Simultaneously, the mean values of hardness in these regions are documented as 2.28 GPa, 2.12 GPa, and 2.08 GPa, respectively, contributing to an aggregate mean hardness for Sample D of 2.16 GPa (as illustrated in **Figure 10a,c**). Region D3 exhibited a normal distribution of Young's modulus and hardness with relatively diminished values, while Region D1 showcased a comparable distribution with relatively elevated values of both Young's modulus and hardness (as depicted in **Figure 10b,d**). However, when combining the data from all three locations, the dual peak pattern distribution persists, highlighting the consistent presence of two prominent peaks or high-frequency regions in the nanoscale distribution of Young's modulus and hardness in Sample D. This suggests a correlation wherein lower values of mechanical properties may be associated with a softer material, while higher values correlate with a harder material.

The consistent observation of a dual peak pattern persists when combining data across all the six samples with 18 different locations and 7,200 data points, indicating two predominant mechanical characteristics at the nanoscale within the shale, as exemplified in **Figure 11a,b**. In the first one, denoted as Phase 1 and characterized by lower values of Young's modulus ranging from 7 to 40 GPa and hardness ranging from 0.3 GPa to 1.6 GPa, there is however a pronounced indication of a softer material. This identification of a softer phase holds significant implications for comprehending the material's response to external forces, particularly those encountered in hydraulic fracturing processes. Conversely, Phase 2 showcases higher values of Young's modulus ranging from 40 to 85 GPa and hardness ranging from 1.6 GPa to 4.9 GPa, suggesting the presence of a harder material within the shale sample. Understanding this harder phase is crucial for thoroughly assessing the

shale's overall mechanical strength. The observed bimodal distribution not only clarifies the shale rock's dual mechanical characteristics but also enhances our understanding of its intricate mechanical behavior at the nanoscale.

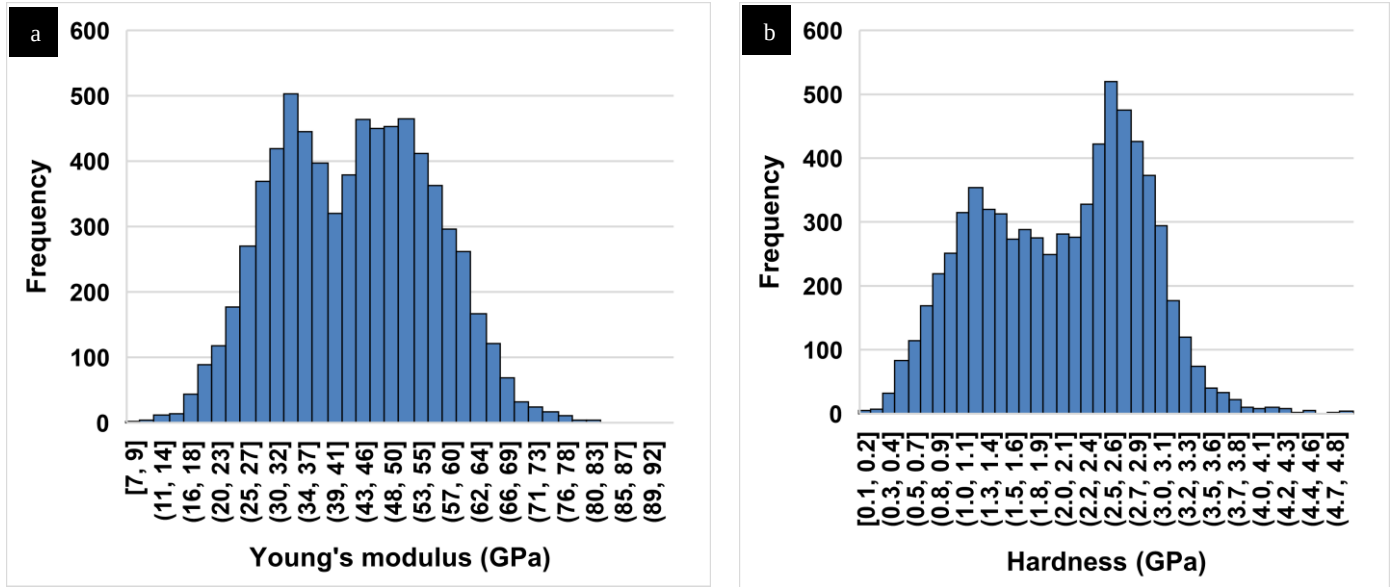


Figure 11. The dual peak pattern distribution of (a) Young's modulus and (b) hardness properties at nanoscale level across all the six sample with 18 different locations

4.3.3 Relationship between nanoscale mechanical properties

The detailed analysis of **Figure 12** provides valuable insights into the interplay between Young's modulus, hardness, and displacement. In **Figure 12a**, the correlation between Young's modulus and displacement is visually represented. The clear inverse relationship between these two factors shows that the displacement decreases as Young's modulus increases. This finding aligns with previous studies (Shi et al., 2020), which have reported similar trends in indentation measurements. Similarly, **Figure 12b** illustrates the relationship between hardness and displacement. As the hardness of the material increases, there is a concurrent decrease in displacement. This aligns with previous research (Shi et

al., 2020). **Figure 12c** explores the correlation between Young's modulus and hardness. A positive correlation is evident, showing that as Young's modulus increases, the material hardness also increases. This finding is consistent with prior studies (Liu et al., 2018, 2023).

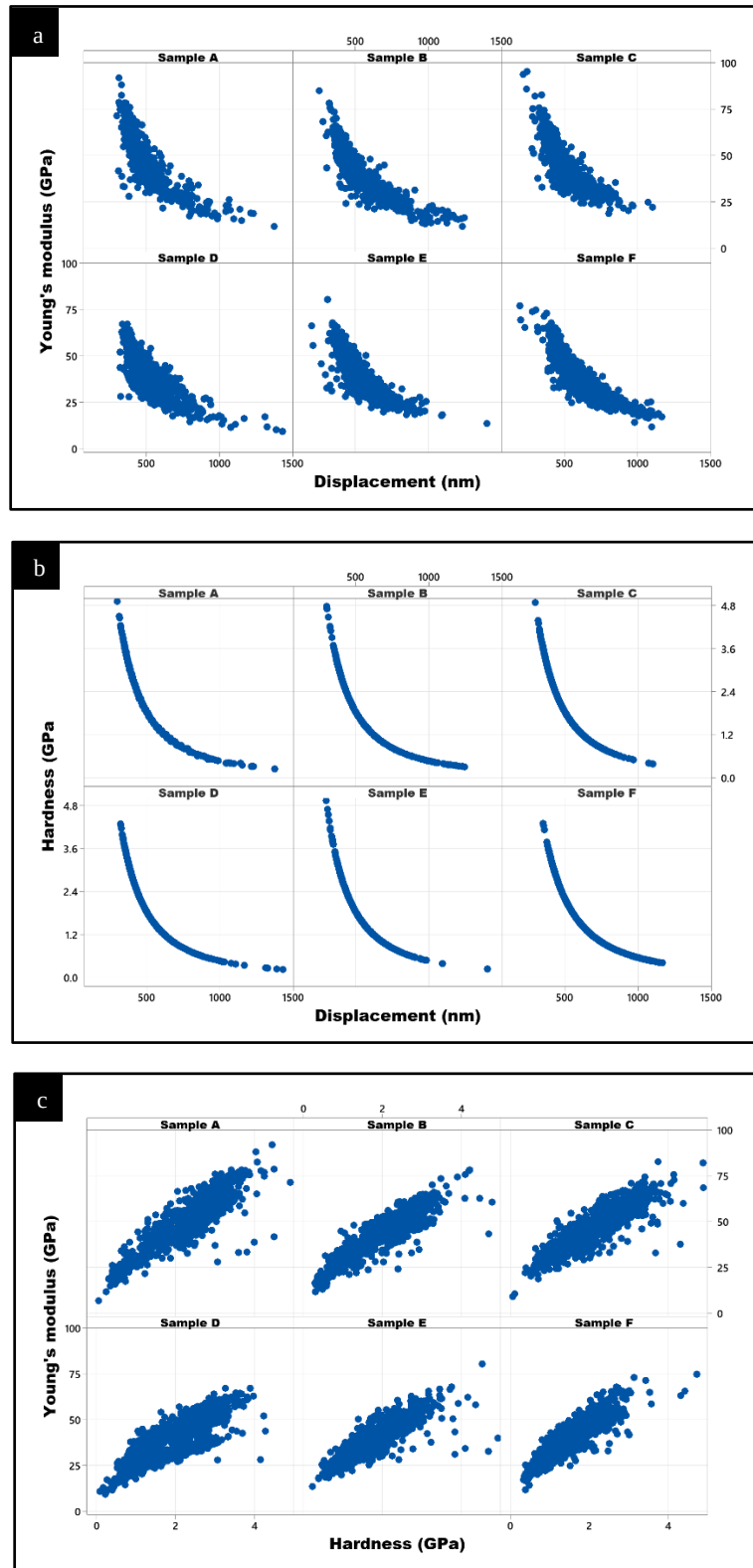


Figure 12. The correlation between (a) Young's modulus and Displacement, (b) hardness and Displacement, and (c) Young's modulus and hardness

4.3.4 Insights from high-resolution imaging of nano-indented spots

The utilization of a fixed force in the indentation process introduces an anticipated variation in displacement depth when indenting different materials (Oliver & Pharr, 2004). The difference in the shape of the imprint indentations becomes evident when different minerals are considered. In our specific case, darker colored area has been identified as organic rich and softer materials, while the whitely colored zones are associated with harder minerals e.g. pyrite, as illustrated in **Figure 13b**. This color variation is related to how SEM

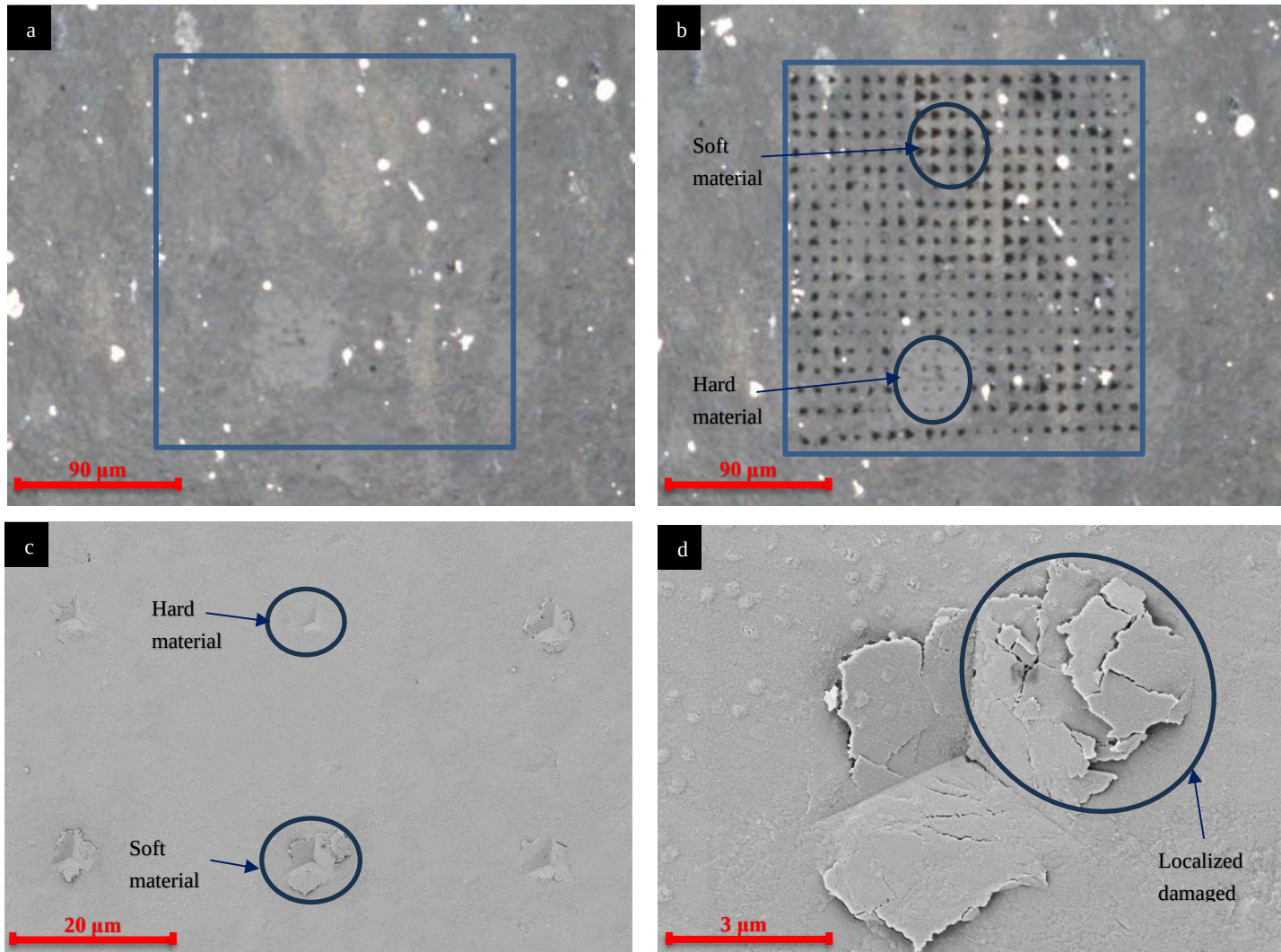


Figure 13. Visualization of Indentation Regions on Sample D through (a) Optical Microscopy before indentation, (b) Optical Microscopy after indentation, (c) SEM Imaging for hard and soft material, and (d) SEM imaging of localized damaged from single representative indentation imprint

micrographs are displayed using a gray scale, within a spectrum from black to white. Pixels/regions with lighter elements are often assigned darker shades of gray (e.g. organic carbon) compared to pixels/regions rich in heavier elements, which are assigned lighter shades of gray (e.g. pyrite). **Figure 13c**. The nano-indentation process induces localized damage in a single indentation imprint, as illustrated in **Figure 13d**, particularly in the softer material region. This analysis provides insights into nano-indentation behavior, reinforcing the earlier identification of two distinct phases at the nanoscale.

4.3.5 *Macroscale mechanical properties*

Before determining the macroscale Young's modulus, we evaluated the surface roughness of the samples. The Root Mean Square roughness (Sq) for Sample C is measured to be 18.09 μm , obtained from a detailed analysis of the rock surface, as illustrated in **Figure 14**. The Sq value is a quantitative indicator of the deviation of the surface profile from its mean line, providing insights into the fine-scale variations in the surface texture.

The mean Young's modulus values ranged from 40.80 to 45.61 GPa across the samples, with the minimum value exhibited by Sample MC and the maximum by Sample MD, as visually depicted in **Figure 15a**. The data points for each sample show a normal distribution, signifying that they are symmetrically spread around the mean. This indicates consistent mechanical properties within each sample. This observation persists when analyzing all six macro samples collectively, as indicated in **Figure 15b**. Furthermore, the 95% Confidence Interval mean values for macroscopic Young's modulus exhibit some convergence in mechanical behavior across all samples. This overlap implies that the true mean values for the macroscopic Young's modulus of different samples are comparable or not significantly disparate (

Table 3). However, uncertainty in the mean values for macroscopic Young's

Sample ID	Frequency	Mean of E (GPa)	Standard Deviation	95% Confidence Interval (GPa)
Sample MA	30	42.15	4.73	(40.10, 44.21)
Sample MB	30	42.04	3.92	(39.99, 44.09)
Sample MC	30	40.8	4.36	(38.75, 42.86)
Sample MD	30	45.61	4.91	(43.55, 47.66)
Sample ME	30	43.03	8.04	(40.97, 45.08)
Sample MF	30	41.92	7.01	(39.87, 43.97)

modulus persists, as indicated by the standard deviation. For instance, Sample MD displays a higher standard deviation, indicating greater variability among measurements, while Sample MC exhibits a lower standard deviation, denoting more consistency in the recorded values.

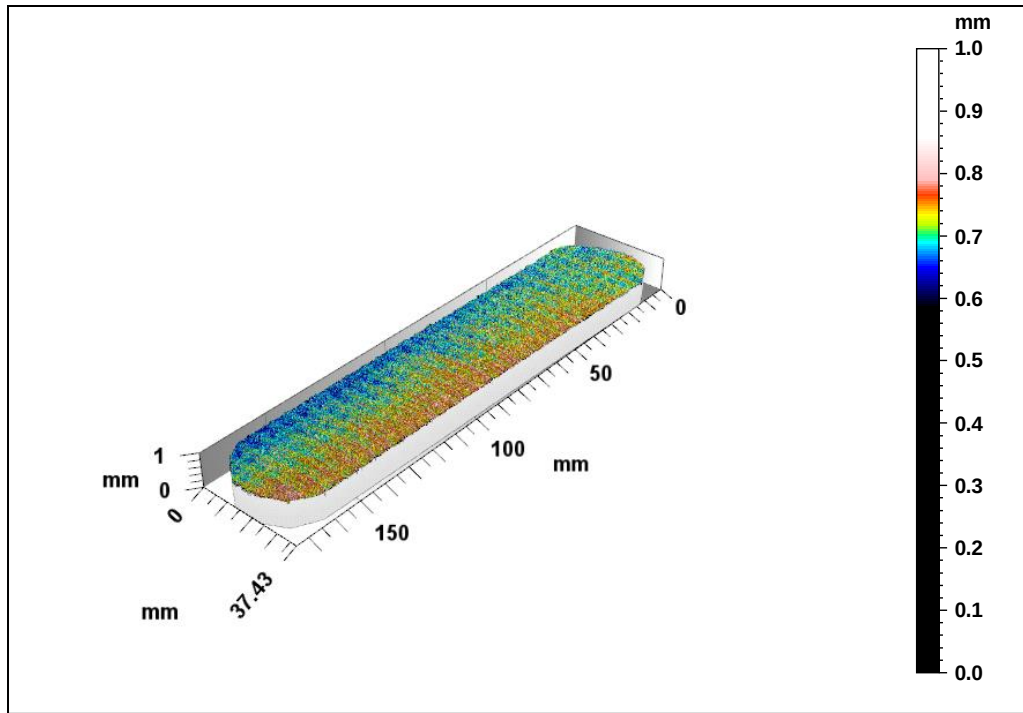


Figure 14. Surface roughness mapping of Sample C

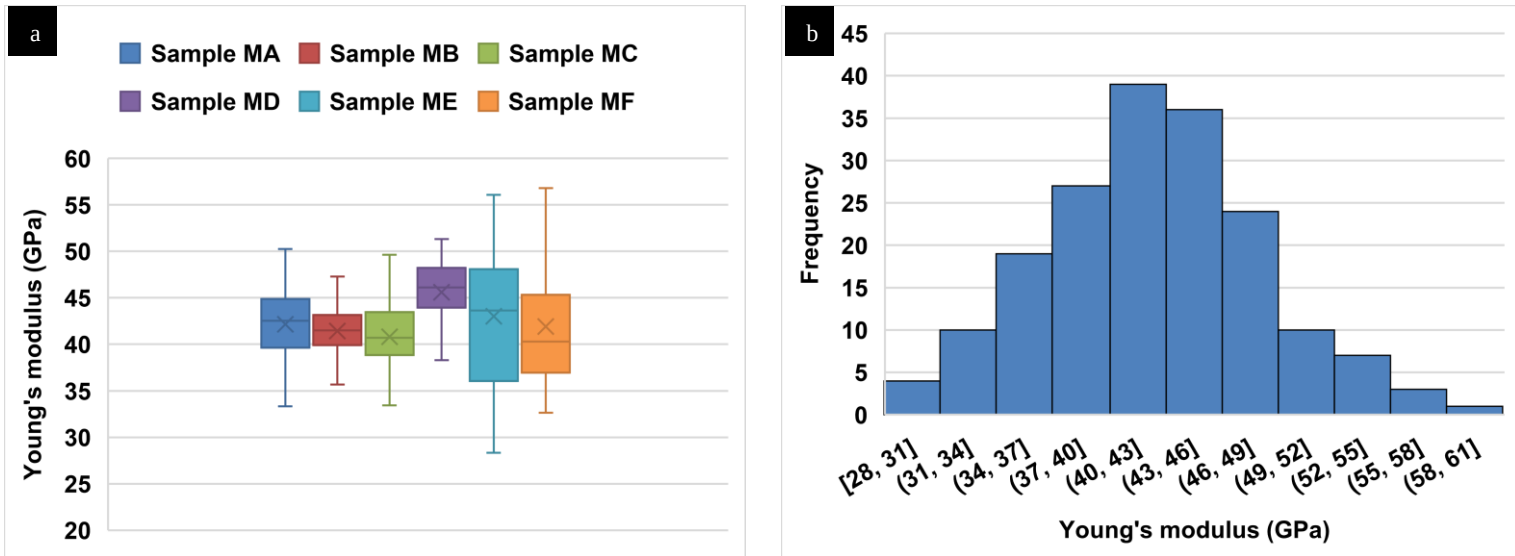


Figure 15. Macroscopic (a) Young's modulus values and (b) distribution of Young's modulus across six large shale samples.

Table 3. Statistical analysis of the mechanical properties of six large samples (MA, MB, MC, MD, ME, and MF) with respect to Young's Modulus (E).

Sample ID	Frequency	Mean of E (GPa)	Standard Deviation	95% Confidence Interval (GPa)
Sample MA	30	42.15	4.73	(40.10, 44.21)
Sample MB	30	42.04	3.92	(39.99, 44.09)
Sample MC	30	40.8	4.36	(38.75, 42.86)
Sample MD	30	45.61	4.91	(43.55, 47.66)
Sample ME	30	43.03	8.04	(40.97, 45.08)
Sample MF	30	41.92	7.01	(39.87, 43.97)

4.3.6 Comparative analysis of nano- and macroscale interrelations

Analyzing the interrelations between nano- and macroscale measurements is crucial for gaining insights into the manifestation of material properties at different scales. Mean Young's modulus at the nanoscale (44 GPa) aligned closely with the macroscale value (42.6 GPa). Nanoscale Young's modulus ranged from 43.7-44.4 GPa (95% CI) with a standard deviation of 13.6, while at the macroscale the range was 40.6-44.6 GPa with a standard deviation of 5.8 (**Figure 16a**).

This proximity of mean values across scales indicates consistency in mechanical properties. A notable distinction emerges in the behavior of the distribution of Young's modulus between nanoscale and macroscale measurements. Specifically, the nanoscale distribution reveals a dual-peak pattern, indicating two prevalent phases in the material's mechanical characteristics. In contrast, the macroscale distribution displays a normal distribution, signifying a more uniform spread of Young's modulus values. This suggests that the macroscopic behavior is controlled by the two constituents (Phase 1 and 2) in a proportionality that is aligned with their frequencies.

The normal distribution of macroscale Young's modulus aligns within the broader spectrum of the nanoscale distribution (**Figure 16b**). The nanoscale distribution covers a more comprehensive range from 7-85 GPa, indicating the ability to capture the full spectrum of the material characteristics, including softer organic substances with a modulus as low as 7 GPa (Bennett et al., 2015). On the contrary, the macroscale distribution is more confined, ranging from 25-60 GPa, representing an average influenced by the diverse minerals encountered during indentation. Additionally, the higher frequency of nanoscale measurements compared to the relatively lower frequency of macroscale

measurements indicates that, with a small sample size, nanoscale measurements offer more opportunities to measure multiple indentations compared to macroscale measurements. This is because macroscale measurements require larger samples to achieve a higher frequency of measurements (Liu et al., 2021). This highlights the unique capabilities of nanoscale measurements to discern specific material characteristics with constrained sample, especially at the lower modulus range.

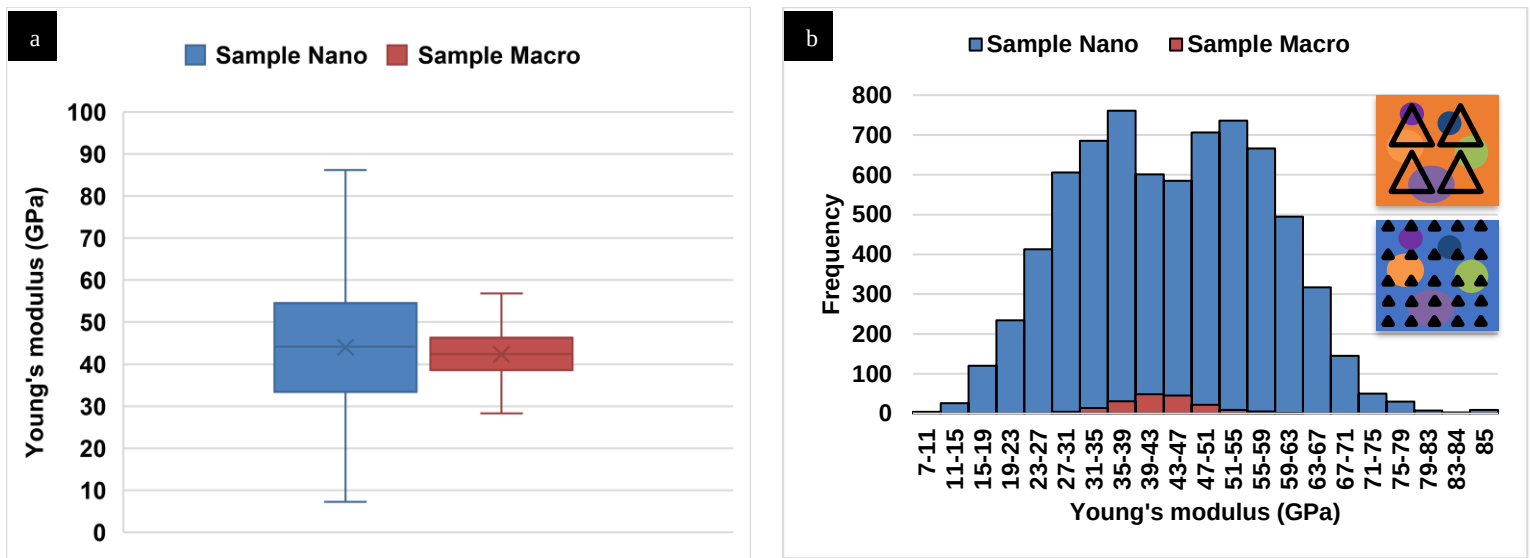


Figure 16. Comparative analysis of (a) Young's modulus values and (b) distribution of Young's modulus obtained from nanoscale and macroscale measurements.

4.3.7 General discussion

The introduction of this paper demonstrates the persistent challenges in establishing a comprehensive understanding of shale's mechanical properties due to the observed discrepancies in previous research outcomes. These variations are often linked to the inherent heterogeneity in mineral behavior within diverse shale formations, leading to different mechanical responses. Like other composites, shale's elastic properties are influenced by its individual components and their interactions. This suggests that, at least

in a qualitative sense, the overall properties of bulk rocks at the macroscale are influenced by the microscale properties of each constituent. Consequently, bridging the gap from observed nanoscale behavior to macroscale outcomes is still unresolved.

While traditional macroscopic mechanical characterization methods are valuable, they face limitations in capturing the intricacies of shale heterogeneity. To address this gap, the study employs nano-indentation as a sophisticated technique, offering a more localized and in-depth exploration of the mechanical attributes of shale. This work focuses on Eagle Ford shale samples, aiming to unravel the mechanical heterogeneity through a dual approach—nano and macroscopic testing supported by SEM imaging. By integrating these methods, the study seeks to establish a robust statistical alignment between the nano and macro-mechanical properties. Experimental results from this study show that there is an alignment of the mean of shale mechanical properties at different scales. A positive mean correlation between nanoscale and macroscale behaviors suggests that phenomena observed at the nanoscale persist in macroscale behavior (**Figure 16**). This alignment is crucial for bridging the gap in understanding how the mechanical behavior of shale constituents translates across different scales. The objective is not only to address the limitations of conventional methods but also to enhance the accuracy of anticipating the mechanical behavior based on the individual constituents. This approach holds promise for advancing our knowledge of shale geomechanics, offering insights that extend beyond conventional macroscopic analyses.

In the context of hydraulic fracturing, a critical consideration arises from the initiation of cracks at the nano- and microscale (Wang et al., 2022), necessitating a cautious approach in the analysis of crack propagation directions and the overall design of hydraulic

fracturing operations. The intricate interplay of geological features at the nanoscale introduces an additional layer of complexity, particularly concerning the anisotropy of the clay matrix (Wu et al., 2020). Variations in rock mechanical properties within these layers may result in non-uniform fracture propagation, thereby impacting the overall efficacy of hydraulic fracturing (Waters et al., 2011). The inherent shale mechanical properties, involving both hard and soft phases at this scale (**Figure 11**), play a crucial role in controlling macroscopic behavior, influencing the macroscale characteristics of the fracking mechanism. This introduces preferences in directionality that may not be obvious when solely considering macroscale attributes. Therefore, the findings of this study on shale mechanical heterogeneity and its correlation across scales provide insights into the mechanisms of crack and fracture propagation in hydraulic fracturing processes within shale formations. As hydraulic fracturing operations evolve, considering these multi-scale factors becomes indispensable for optimizing fracture design strategies.

Unlike conventional approaches that rely on various upscaling models to derive the overall properties from nano/micro-scale mechanical data (Li et al., 2019), the newly proposed cross-scale indentation technique can directly correlate between nano and macroscale properties. This eliminates the uncertainty of upscaling models and offers the potential for direct measurements, providing a more straightforward and potentially more accurate understanding of shale mechanical properties.

4.4 Conclusions

In this study, we used the nano-indentation method alongside macroscale testing to investigate the mechanical heterogeneity of organic-rich shales, complemented by SEM

imaging. The characterization analysis of mineral and elemental compositions revealed Pyrite and Dickite as the top two dominant mass percentages, with primary elemental components identified as Fe, Si, S, and Al. Nanoscale results showed a dual-peak distribution indicative of soft and hard materials validated through SEM imaging. Young's modulus and hardness properties at the nanoscale vary between 7 and 85 GPa and 0.3 and 4.9 GPa, respectively. In contrast, macroscale yield exhibited a normal distribution for Young's modulus values ranging from 25 to 60 GPa, representing the overall mechanical behavior on a macroscopic scale. Notably, the nanoscale distribution exhibited a wide range of Young's modulus, while the macroscale showed a narrower range, with the macroscale distribution falling within the nanoscale distribution. The comparative study between nanoscale and macroscale results revealed a closely aligned mean value for Young's modulus, with the nanoscale at 44 GPa and macroscale at 42.6 GPa. These findings propose a promising integration of nano-indentation methods and macroscale testing for a comprehensive analysis of rock mechanical properties, establishing valuable correlations between nano- and macroscale results which holds a promise for enhancing the success of hydraulic fracturing operations in unconventional shale plays.

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CHAPTER 5 NANOSCALE ASSESSMENT OF SHALES

MECHANICAL INTEGRITY UPON INTERACTIONS

WITH SUPERCRITICAL CO₂²

Abstract – Supercritical carbon dioxide (sc-CO₂) injection into shales holds a promise for multiple benefits, including carbon geo-storage, enhanced hydrocarbon recovery, and serving as a more environmentally friendly alternative to water-based fracking fluids. Assessing the mechanical response of shales to sc-CO₂ injection is crucial for optimizing these operations. Utilizing nano-indentation, this study comprehensively evaluated the mechanical response of organic-rich Eagle Ford shale samples to sc-CO₂ exposure, establishing a baseline understanding prior to and following sc-CO₂ aging. Moreover, the mechanical assessment was complemented by Scanning Electron Microscopy (SEM) imaging to visualize morphological alterations. The samples were subjected to aging under sc-CO₂ conditions for 7, 30, and 60 days. The samples exhibit an average value of 6.17% TOC, which is generally considered rich in organic matter. The results demonstrated a gradual weakening of the shale matrix with increasing sc-CO₂ exposure duration. Notably, the average nano-indenter displacement under a fixed force increased by 14.1% after 7 days, 33.2% after 30 days, and 44.7% after 60 days compared to the initial value. This trend confirms the weakening effect of sc-CO₂ on the shale's mechanical properties. This study is crucial to evaluating the mechanical interactions between sc-CO₂ and shales for a number of critical subsurface operations such as stimulation processes, and long-term carbon geo-storage for an improved reservoir-scale implementation.

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5.1 Introduction

Organic-rich shale is a sedimentary rock that contains organic matter, primarily composed of fossilized marine and terrestrial plants and animals (Kanitpanyacharoen et al., 2012). Shale is labeled as organic-rich when its Total Organic Carbon (TOC) content is 2% or more (Wood & Hazra, 2017). These rocks are typically composed of fine-grained clay minerals and are known for their extremely low permeability and low porosity (Seiphoori et al., 2017). The exploration and exploitation of shales have witnessed a paradigm shift with the introduction of the innovative techniques of lateral drilling and hydraulic fracturing, allowing for transforming shales into reservoirs capable of producing hydrocarbons at economic rates. Since then, efforts have been made to enhance hydrocarbon production through optimizing hydraulic fracturing operations while minimizing negative impacts on the environment (Jia et al., 2019; Memon et al., 2022; Wang et al., 2019). In this context, supercritical carbon dioxide (sc-CO₂) emerged as a viable alternative to water in hydraulic fracturing operations for the development of unconventional reservoirs due to its unique properties such as its thin consistency, excellent gas-like diffusion, and liquid-like density (Wang et al., 2019; Zhang et al., 2017; Zhou et al., 2018), which allows CO₂ molecules to easily spread into micro-fractures (Deng et al., 2018; Zhang et al., 2017). In addition, utilizing sc-CO₂ reduces the reliance on detrimental chemicals and additives commonly linked to traditional hydraulic fracturing processes, such as biocides and surfactants (Middleton et al., 2014). These studies were mostly carried out with sc-CO₂ being the basis of hydraulic fracking fluids and benchmarked against the

performance of typical slick water. It was reported that sc-CO₂ fracking efficiency was not as favorable as the case of water (Al Shafloot et al., 2021). However, this benchmarking is based on replicating water-based fracking while overlooking the long-term effect of CO₂ rock interactions. Such chemical and physical interactions could shift mechanical behavior and subsequently influence fracturing efficiency (Ao et al., 2017; Wang et al., 2018). The timeframe to capture these effects is beyond the immediate initiation of hydraulic fractures. Moreover, the significance of understanding CO₂-shales interactions from the mechanical perspective is not limited to enhancing stimulation efficiency but also is critical for carbon geo-storage as the mechanical integrity influences the sealing capability, where shales are one of the primary seals of subsurface reservoirs.

In contrast to conventional formations, shales exhibit more sophisticated geomechanical properties (Villamor et al., 2016). The anisotropic nature of shale's matrix leads to variations in strength parameters and deformation behavior (e.g., Poisson's ratio and the strength of shale rock) (Wu et al., 2020; Zhao et al., 2023). In previous studies (e.g. Aoudia et al., 2010; Yin et al., 2017; Zhao et al., 2017), the mechanical properties of shale were found to be sensitive to several factors, including organic content, mineralogy, heterogeneity, and temperature (Chen et al., 2019; Li et al., 2016). Moreover, interactions with sc-CO₂ can introduce additional complexities to the already multifaceted mechanical behavior of shales (Dong et al., 2022; Fatah et al., 2020).

To date, limited information exists about the alterations in the mechanical properties of organic-rich shale treated with sc-CO₂, attributed to the resolution constraints of conventional tests. Using traditional testing, previous studies reported a clear reduction in shale strength when expose to sc-CO₂ (Ao et al., 2017; Lyu et al., 2016; Yin et al., 2017).

Through the utilization of Brazilian splitting strength (BSS), it was observed that the reduction of shale strength by 46% due to sc-CO₂ saturation time and bedding orientation underscores the pivotal role of pore structure damage in the mechanical degradation induced by sc-CO₂ (Feng et al., 2019). This conventional testing presents challenges, including the instability of shale's physical and chemical characteristics complicating coring, the time-consuming and costly nature of conventional mechanical tests lacking repeatability, and the necessity for an effective method to analyze fluid seepage effects on mechanical properties across diverse mineral distributions pre- and post-sc-CO₂ treatment (Shi et al., 2020). However, the introduction of an advanced high-resolution technique, nanoindentation, has solved the problem and facilitated a precise assessment of mechanical properties at the nanoscale (Wilkinson et al., 2015). Nanoindentation is a simple process of applying a predefined force to penetrate the material's surface with a small tip, and measuring the resulting deformation (Oliver & Pharr, 2004). The technique has numerous applications in areas such as materials design, biomaterials, and surface engineering to understand the nanoscale mechanical characteristics of small chips specimens (Fischer-Cripps & Nicholson, 2004; Schuh, 2006; Shukla et al., 2015). Nanoindentation provides a valuable technique for examining the mechanical properties of shales at the nano-scale, particularly in assessing mechanical changes in organic-rich shales where extended exposure to sc-CO₂ has not been studied extensively (Kong et al., 2021; Lucca et al., 2010). Prior studies have predominantly concentrated on characterizing alterations occurring within specific nanoscale regions, with shale samples typically subjected to exposure durations limited to a maximum of 48 hours (Kong et al., 2021; Shi et al., 2020; Shukla et al., 2013). This study aims to establish a solid framework for understanding the changes in

mechanical integrity resulting from prolonged exposure to sc-CO₂ and to comprehensively characterize the entirety of shale formations.

The complexities inherent in nanoscale behavior, the absence of standardized testing procedures, and limited methodologies for a thorough mechanical analysis of shale interacting with CO₂ have contributed to a notable degree of uncertainty regarding the mechanical attributes of shale. The objective of this study is thus, to conduct a thorough assessment of shale's mechanical alterations upon long-time exposure to sc-CO₂ at the nanoscale level. The experimental work was conducted on shale samples from Eagle Ford. The remainder of the paper is organized as follows. The methodology is outlined, detailing the different phases of the experimental work. This is followed by results and discussion. The paper is then concluded with some remarks and future recommendations.

5.2 Methodology

5.2.1 Workflow

The workflow began with the crucial step of sample preparation, forming the foundational basis for subsequent analyses as detailed in **Figure 17**. During this phase, the shale specimen underwent through several processes, including cutting and surface polishing, ensuring optimal readiness for further investigation. Additionally, a rigorous cleaning process was implemented to eliminate potential contaminants, and high-resolution imaging technique were applied to confirm the specimen's suitability for in-depth analysis. Following the sample preparation, the workflow advanced through subsequent stages encompassing mineralogical, elemental, and rock evaluation experiments. Subsequently, the samples underwent detailed mechanical tests at the nanoscale. These testing procedures aimed to acquire a comprehensive characterization of the rock's mechanical response and

behavioral tendencies, with subsequent repetitions after sc-CO₂ aging. The workflow was concluded with data benchmarking before and after sc-CO₂.

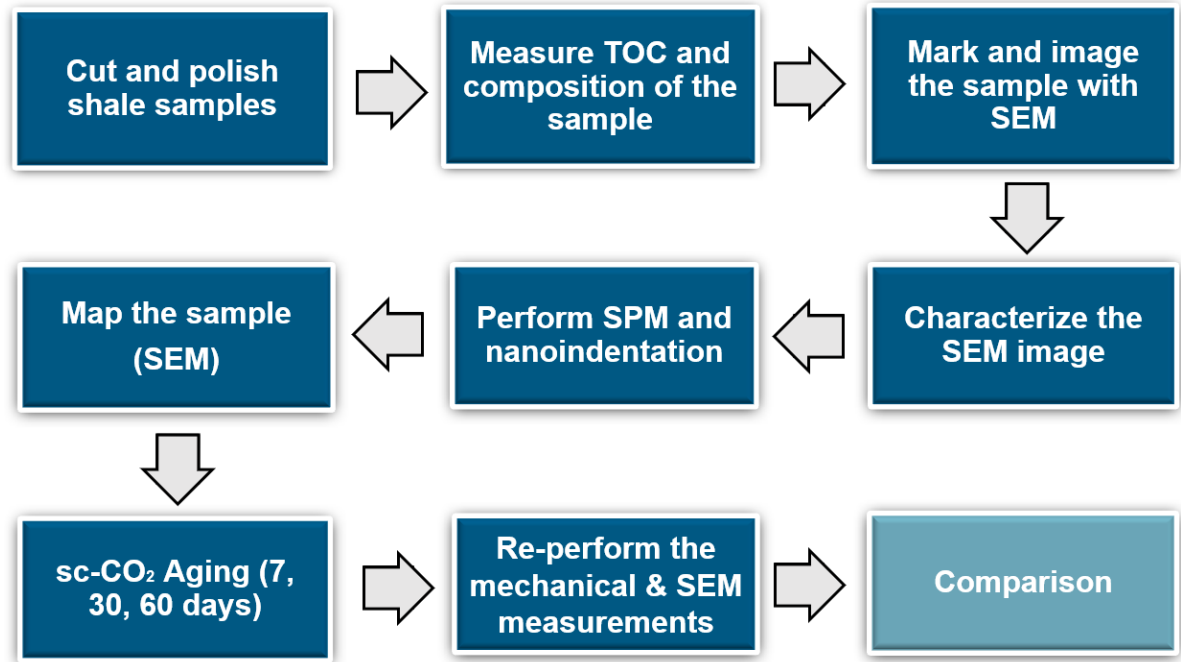


Figure 17. Workflow designed to assess the nanoscale mechanical properties of shale.

5.2.2 Sample Preparation

Three micro cylindrical shale samples were carefully prepared for nanoscale testing. The samples underwent a two-step polishing process, involving both mechanical and ion beam techniques, to reduce surface roughness in preparation for nanoindentation testing and to enable clear visualization under SEM. In the mechanical polishing stage, the cylindrical specimens, originally 1.5 inches in diameter and 3 inches in length, were cut into smaller pieces, each measuring 1 cm in diameter and 0.5 cm in length, using Delta Petrocut (Buehler) and EM TXP (Leica) equipment. To achieve a mirror-like surface, the three micro-samples were subjected to a series of polishing steps, starting with 30 μ m and

15 μm silicon carbide paper, followed by finer diamond lapping foil in stages from 9 μm to 0.5 μm . Before ion milling, thoroughly clean the sample to remove any residues from the previous mechanical preparation. The cleaning procedure, employing the ion beam EM TIC 3X (Leica), incorporates specific parameters, including an incident angle set at 15° , an accelerating voltage of 5kV, a duration of 15 minutes, medium rotation, and lateral movement within a range of ± 5 mm. Subsequently, ion beam polishes the specimens with an incident angle of 4.5° , accelerating voltage of 6kV, total processing time of 120 minutes, medium rotation, and lateral movement within a range of ± 5 mm. In order to address potential sample evaporation, a milling duration of 10 minutes was followed by a subsequent cooling period of 10 minutes. This sequential process was consistently repeated until the cumulative milling time reached 120 minutes, effectively mitigating the impact of sample evaporation and yielding a mirror-like surface sample for further analysis.

5.2.3 *X-ray Diffraction, X-Ray Fluorescence and rock evaluation experiments*

The mineralogical and elemental composition of the samples were determined through X-ray diffraction (XRD) and X-Ray Fluorescence (XRF) techniques (Amao et al., 2022). The analysis of the prepared samples via XRD was conducted using a Panalytical Empyrean instrument operating under the conditions of 45 kV and 40 mA, employing $2\theta/\theta$ -scanning methodology. Furthermore, XRF analysis was performed using the M4 TORNADO system (μ -XRF: Bruker Nano GmbH) featuring a micro-focused rhodium source. The instrument operates at 50 kV and 600 μA , with a polycapillary optic providing an approximate spot size of ~ 20 μm . Additionally, Total Organic Content (TOC) was assessed using the Rock-Eval 6 setup (Carvajal-Ortiz & Gentzis, 2015). In preparation for these analyses, rock chips were subjected to crushing processes, yielding particle sizes

below 4 μm (Locock et al., 2012). The integration of these analytical methods yielded thorough insights into the mineralogical composition and elemental ratios of the samples.

5.2.4 *Nanoscale experimental design*

Nano-indentation methodology and principles have been previously documented (Fischer-Cripps & Nicholson, 2004; Oliver & Pharr, 1992). In a typical experiment, a controlled load is applied to the sample, specifying either force or depth, followed by unloading to generate a force-depth hysteresis curve that reveals micro-scale mechanical properties based on parameters like force and contact depth (Zeng et al., 2018). Here, a Hysitron TI 980 nanoindenter (Hysitron, Inc.) facilitated testing to obtain the specimens' mechanical properties. Integrated scanning probe microscopy (SPM) enabled surface roughness assessments to ensure adequacy before testing (Du et al., 2018; Lucas et al., 1998).

Systematic rectangular nano-indentation arrays were generated on the polished sample surfaces using a 10 mN-loaded Berkovich diamond probe ($E = 1140 \text{ GPa}$, $\nu = 0.07$) at ambient temperature and 10 μm spacing. Each sample area underwent a 20×20 array (400 indentations), with location indentations facilitating optical microscopic identification post-testing. To provide statistical representation, measurements were conducted in triplicate at random locations across each micro-sample, yielding 1,200 total indentations per sample. Subsequent scanning electron microscopy (Zeiss Crossbeam 550) enabled morphological assessments before aging the specimens in supercritical CO_2 at 13.8 MPa and 75°C for 7, 30, and 60 days.

5.3 Results and Discussion

5.3.1 *Rock composition*

The specimens were subjected to various assessments of their material and mechanical characteristics prior to their interaction with sc-CO₂. A thorough analysis, incorporating XRD, XRF, and rock assessment experiments detailed in Section 2.1.2, was conducted. The outcomes of these examinations unveiled a predominant mineral composition, with 87.1% Calcite, 11.7% Quartz, 0.9% Pyrite, and 0.2% Muscovite, accompanied by primary elemental components identified as Ca, Si, S, and Fe, as delineated in **Figure 18-a**, and **b**. The specimens have on an average TOC content of 6.17%, indicative of a significant presence of organic matter, aligning with the characteristic profile of organic-rich shales (Speijer & Wagner, 2002). The compositional analysis substantiated the potential of chemical and physical alterations of shale's matrix upon the introduction of sc-CO₂. The presence of iron-based minerals such as pyrite could lead to active dissolution/precipitation through a thermodynamically controlled series of reactions, while organic matters are anticipated to undergo a rapid swelling effect induced by the adsorption of CO₂.

5.3.2 *Statistical representation of nanoindentation*

As delineating the nanoscale effect of sc-CO₂ on shale's mechanical integrity is the primary objective of this study, establishing valid pre- and post-exposure benchmarking methods is crucial. While nano-indentations reflect localized mechanical responses based on the mineralogy of the penetrated location, averaging data collected from random spots can reduce such variations. In this study and based on our observations, it was found that mapping a given sample on three spots using consistent applied force of 10 mN where each

consists of 400 data points yielded a statistically sufficient representation across all samples. Convergence was achieved roughly after 1000 indentations, which correlates with a displacement of 460 nm as shown in **Figure 19**. This number of indentations is considered suitable for benchmarking data (i.e. after exposure to sc-CO₂).

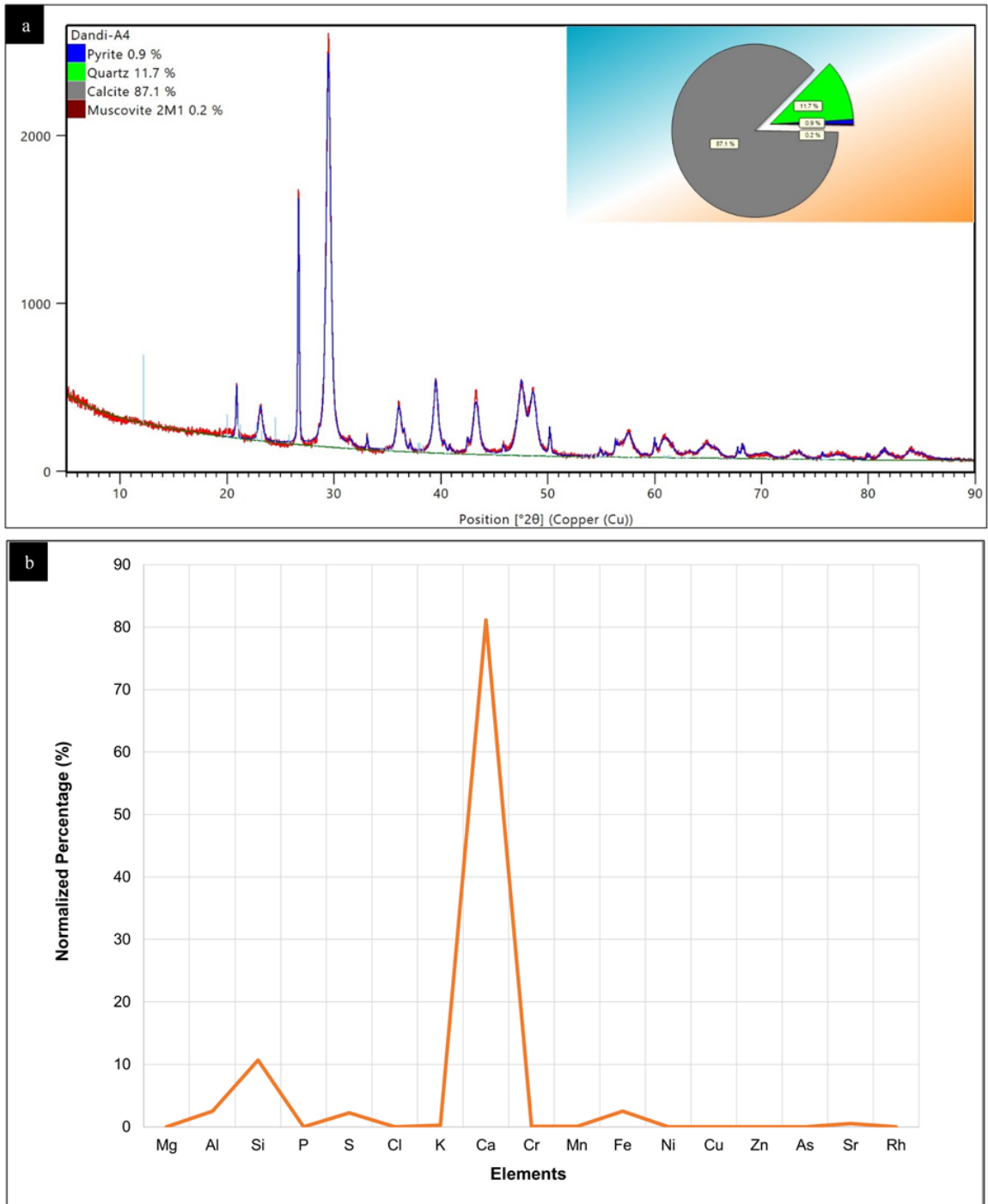


Figure 18. Result of (a) XRD and (b) XRF tests

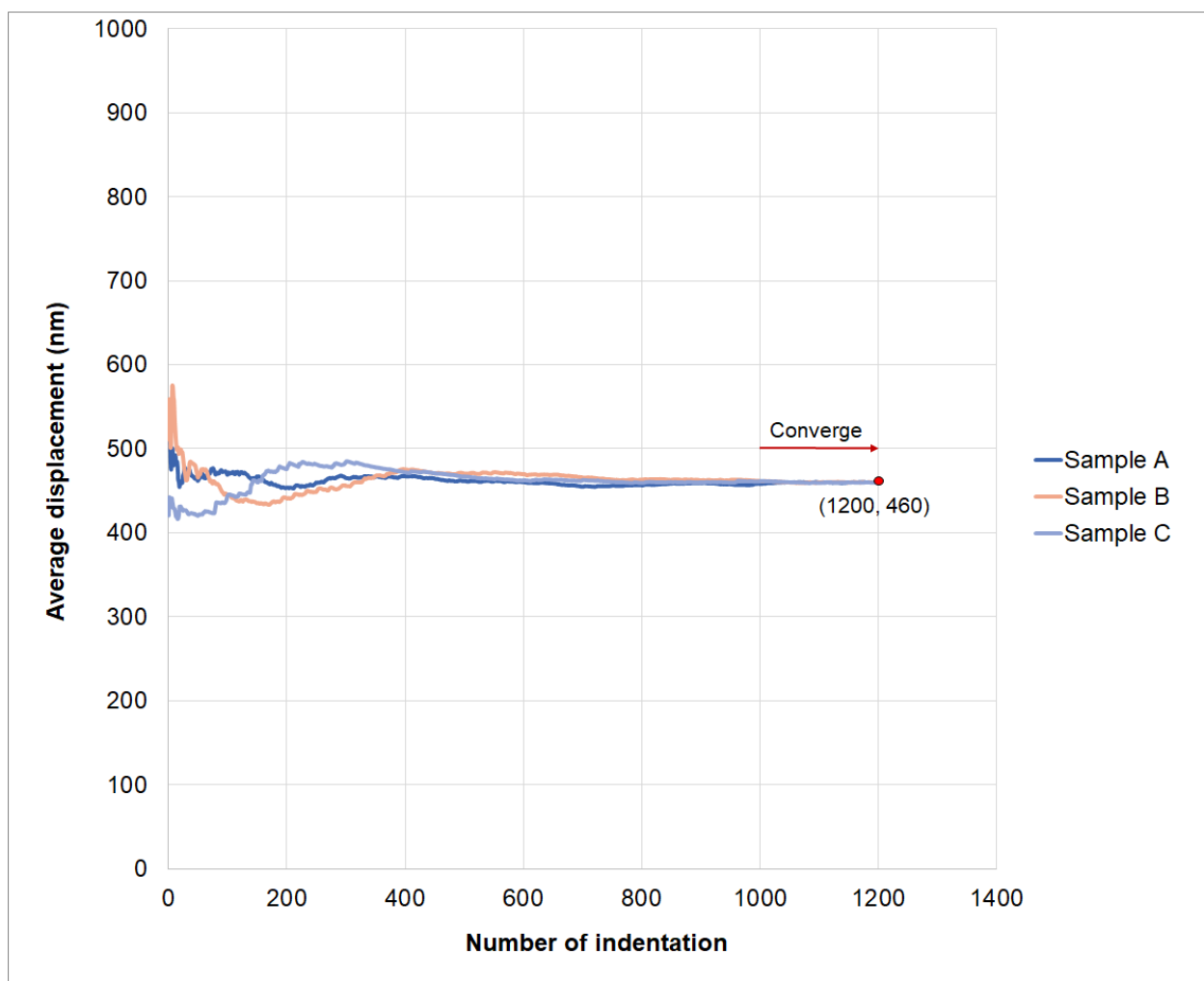


Figure 19. Statistical analysis on the number of indentations in relation to average displacement before sc-CO₂ exposure.

5.3.3 Post-interaction with supercritical carbon dioxide

The evaluation of the mechanical properties of shale after interaction with sc-CO₂ was conducted similarly. Applying a consistent force of 10 mN, the shale rock exhibits progressive deformation during distinct intervals of CO₂ saturation, as illustrated in **Figure 20**. Following a 7-day duration, the displacement increased by 14.1%, relative to the initial average displacement of 460 nm. Subsequently, at day 30, a more pronounced deformation was observed, with a 33.2% increase in displacement. Expanding the analysis to 60 days

demonstrated a continued upward trend in displacement, reaching 44.7%. This sustained deformation trend suggests an ongoing alteration in the mechanical characteristics of the shale rock. The nano-indenter penetrates deeper over time with the same applied force, indicative of a weakening trend induced by prolonged exposure to CO₂. This continuous deformation over time signifies potential modifications in the mechanical features of the shale rock, with deeper indentation depths generally suggestive of diminished material strength. The reduced strength observation aligns with some prior studies (Lyu et al., 2016; Wang et al., 2019).

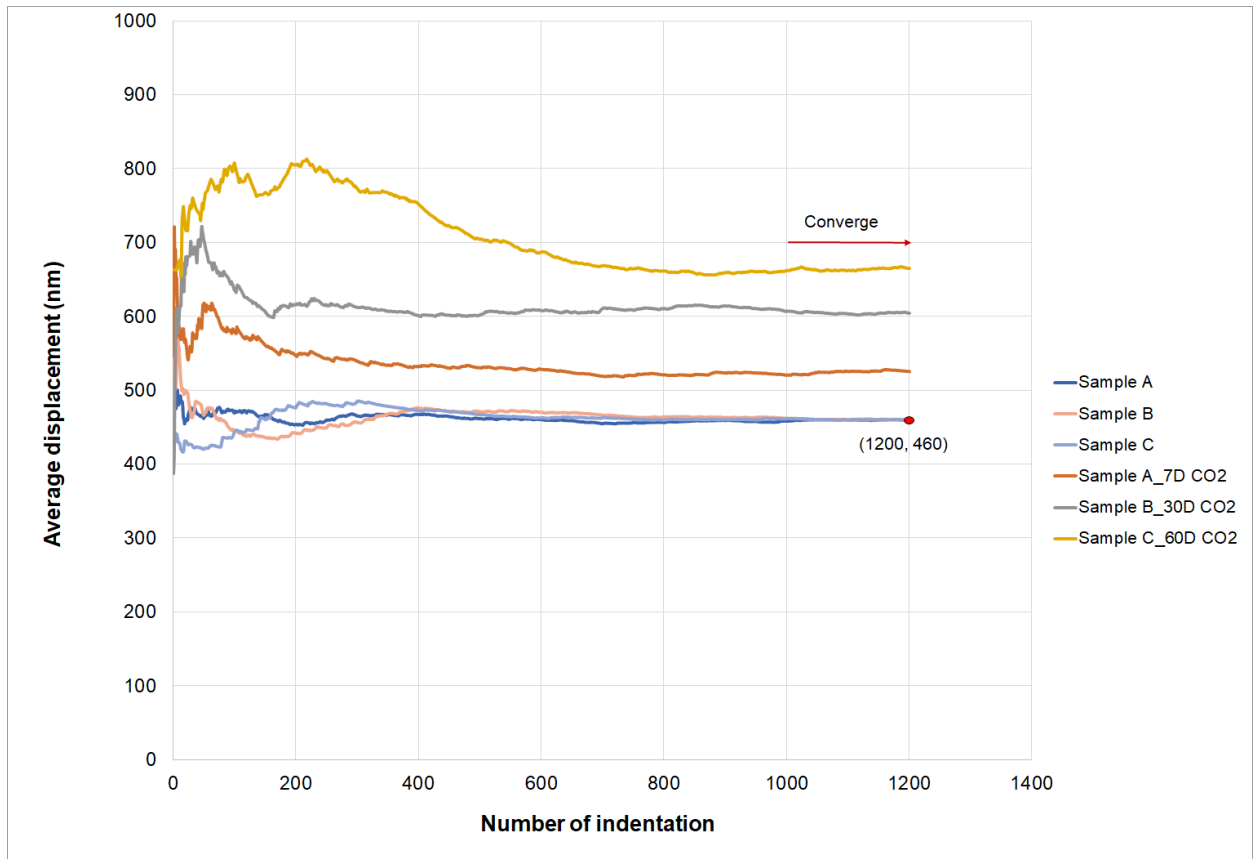


Figure 20. Results of nanoindentation test after sc-CO₂ interactions.

5.3.4 *Surface investigation on supercritical carbon dioxide interaction*

Figure 21 shows a secondary electron image of the area of indents on sample A. The utilization of a fixed force in the indentation process introduces a variation in displacement depth when indenting different materials (Oliver & Pharr, 2004). The difference in the shape of the imprint indentations becomes evident when diverse minerals are considered. In this specific case, darker-colored areas are most likely identified as organic-rich and softer materials, while the whitely-colored zones are associated with harder minerals e.g., pyrite, as illustrated in **Figure 21-b**. This color variation is related to how stereomicroscope on the nanoindenter and SEM micrographs are displayed using a gray scale, within a spectrum from black to white. Pixels/regions with lighter elements are often assigned darker shades of gray (e.g., organic carbon) compared to pixels/regions rich in heavier elements (**Figure 21-c**), which are assigned lighter shades of gray (e.g., pyrite). The nanoindentation process induces localized damage in a single indentation imprint, as illustrated in **Figure 21-d**, particularly in the softer material region.

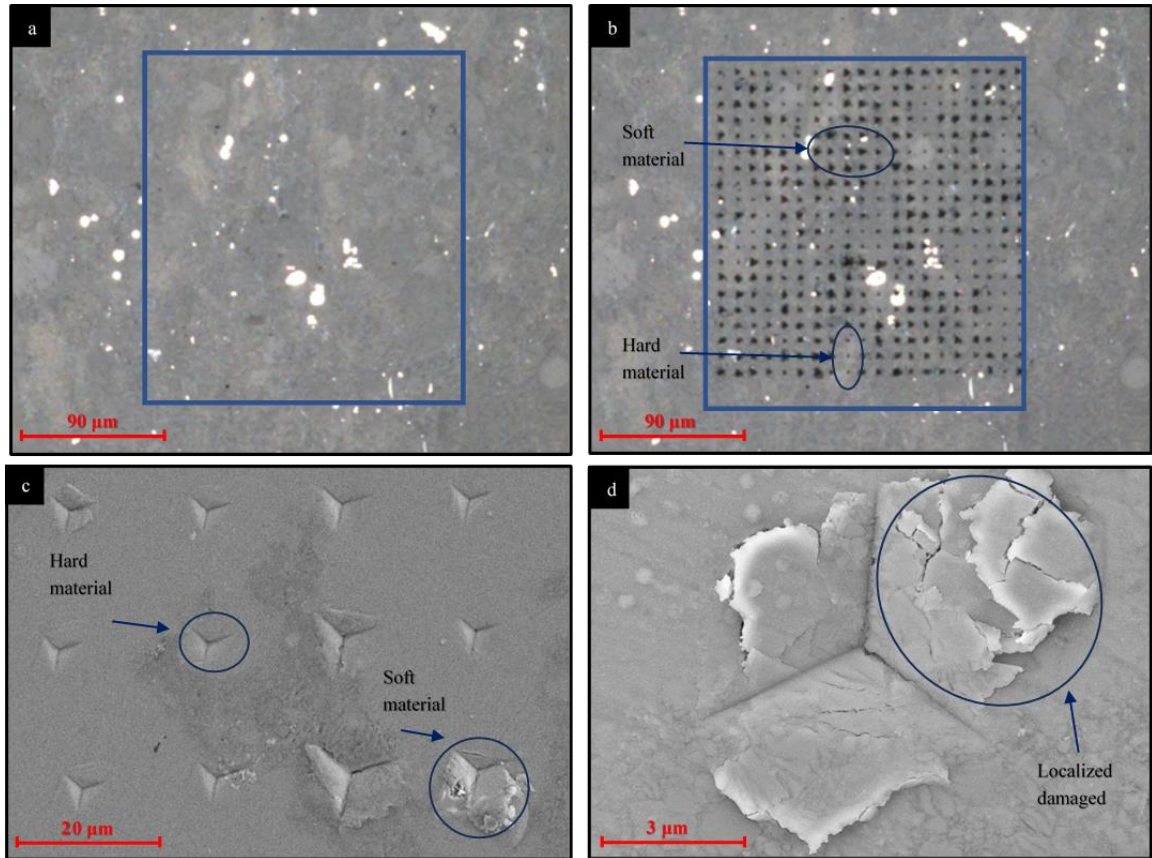


Figure 21. Visualization of Indentation Regions on Sample A through (a) Optical Microscopy before indentation, (b) Optical Microscopy after indentation, (c) SEM Imaging for hard and soft material, and (d) SEM imaging of localized damaged from single representative

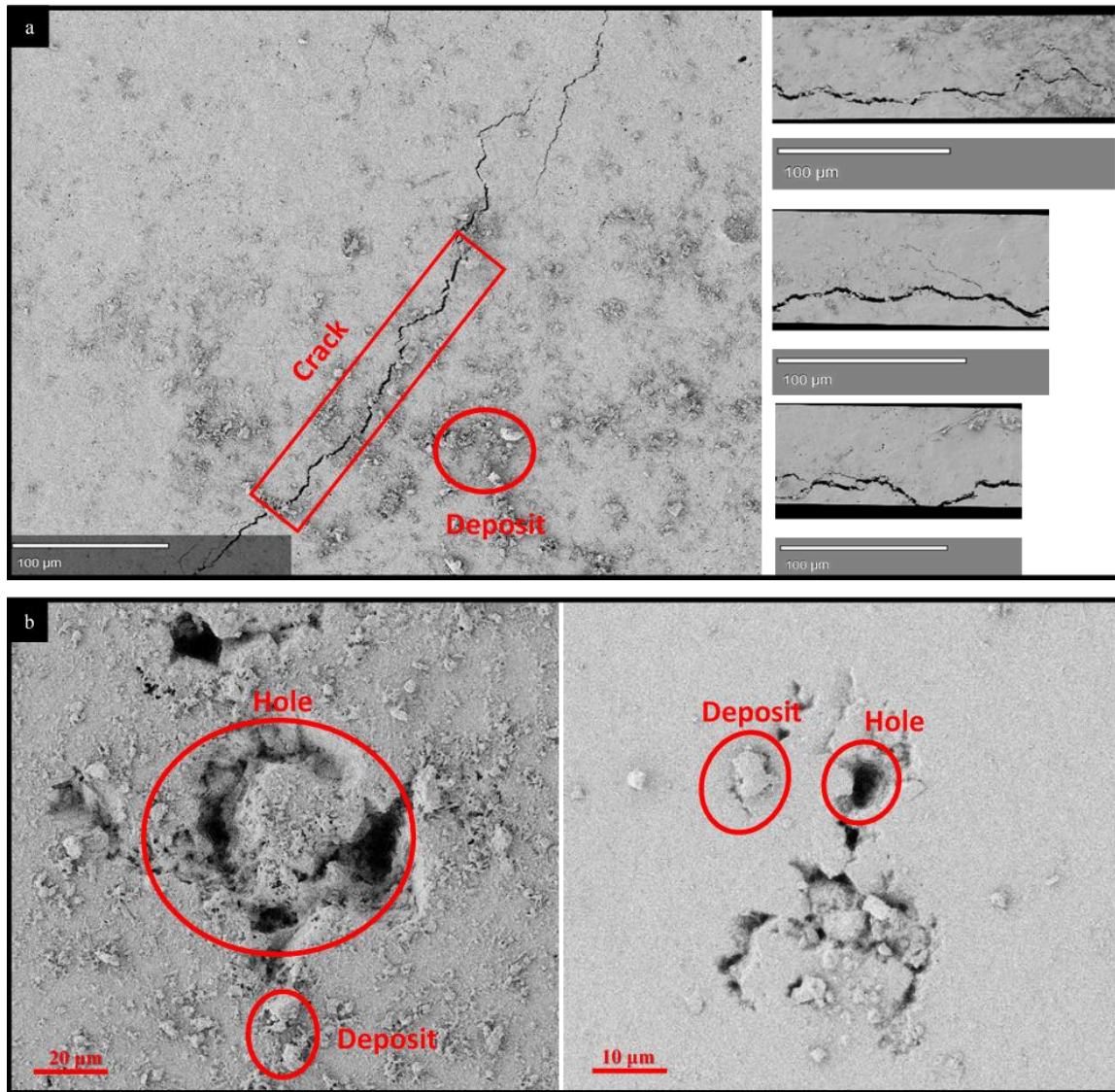


Figure 22. SEM surface images post-interaction with supercritical carbon dioxide, depicting (a) cracks on Sample B, (b) holes, and deposited material on Sample C.

Following a 30 to 60-day exposure to sc-CO₂, significant longitudinal cracks emerged on the shale surface. These cracks substantiate a reduction in material strength, as illustrated in **Figure 22-a**. The SEM surface images, obtained after the specified sc-CO₂ exposure period, revealed the presence of both holes and deposits. The interpretation of these findings indicates material's surfacing, leading to the formation of holes.

Additionally, released precipitates during sc-CO₂ exposure are observed to be deposited in various surface locations, as depicted in **Figure 22-b**. These observations are well aligned with the outcome of the mechanical integrity mapping in the previous section.

5.3.5 Chemical and physical alterations upon interactions with CO₂

The underlying mechanisms of CO₂ – shale interactions involve potential physical and chemical alterations, as highlighted earlier. In the supercritical state, CO₂ exhibits properties of both liquids and gases. It has high fluidity, allowing it to penetrate shale formations more effectively than traditional fluids (Kang et al., 2011). This enhanced fluidity is crucial for reaching remote areas within the shale rock, creating a rich medium for equilibrium-based complex reactions evolving through a series of intermediate compounds leading to dissolution and precipitation, as revealed by surface imaging. Moreover, physical interactions in the organic matters driven by the affinity toward carbon dioxide led to active sorption, within the shale matrix (Bhuiyan et al., 2020). Attributed to its elastic characteristics, organic matters, particularly kerogen, undergoes a swelling effect upon intaking CO₂ (Eckert et al., 1996). In a prior study (Alafnan, 2022), a molecular representation of kerogen was subjected to a combination of molecular dynamics and Gibbs Monte Carlo simulations to delineate structural changes within the organic matters upon introducing sc-CO₂ to the system. A noticeable swelling effect was observed. The molecular simulation assessment was extended to mechanical assessment of stress-strain relationship. It was observed that kerogen interactions with CO₂ led to significant degradation in its mechanical behavior, which is consistent with the findings of this study. Moreover, time evolution showed a sustained deformation trend, signifying an alteration

in the mechanical structure of the shale rock. Thus, these phenomena are strongly correlated with a weakening trend induced by prolonged exposure to CO₂.

5.3.6 General Implications

In the context of hydraulic fracturing, a critical consideration arises from the creation of cracks (Wang et al., 2022), necessitating a cautious approach in analyzing optimized crack creation and the overall design of hydraulic fracturing operations. Nanoindentation testing was employed to examine the mechanical degradation upon interactions with CO₂. Post sc-CO₂ interactions, observable cracks, holes, and deposits indicate softer mechanical strength, making the creation of multiple fractures easier. The existence of defects and micro-fractures post sc-CO₂ interactions contributes to a decline in mechanical properties, reflecting lower fracture energy required for initiation. This is advantageous for achieving lower fracture breakdown pressure and generating a complex fracture network, as suggested by the findings of this study. As a result, injection of sc-CO₂ could be proposed as a pre-fracking phase to enhance the vulnerability of the formation to form a richer network of fractures upon stimulation. At the same time, the injection of CO₂ could serve the purpose of mitigating greenhouse gas emissions, minimizing water usage, and enhancing the ultimate recovery through potential desorption of hydrocarbons.

Moreover, geo-storage of CO₂ has been an active area of research. It is well-documented that the process of geological storage undergoes dissolution in liquids, solids or free phases. The latter relies on the sealing capability of natural entrapments such as shales. The outlined findings of this study draw attention to potential degradation of shale

over time. Hence, long-term storage project should be carefully assessed to ensure successful and safe entrapment of CO₂.

5.3.7 Future Work

This study suggests expanding both experimental and computational investigations to explore other mechanisms, such as mineralization in shale with water and supercritical carbon dioxide (sc-CO₂). Additionally, it is recommended that the impact of temperature on the mechanical behavior of organic matter be examined. The authors plan to employ more practical approaches in upcoming work to better understand changes in both surface and pore networks at the nanoscale, facilitating practical applications. The focus will be on understanding the alteration of minerals in shale/water/sc-CO₂ systems, particularly the interactions between organic matter and brine/CO₂. Moreover, there is a potential for establishing new technologies that offer a valuable set of frameworks for real-world applications based on the novel findings of shale and CO₂ interactions.

5.4 Conclusions

This paper presents long-term tests where Eagle Ford shale samples were exposed to supercritical carbon dioxide (sc-CO₂). Mechanical testing procedures, complemented with scanning electron microscopy (SEM), were used to assess the mechanical changes in the organic-rich shale rocks at the nanoscale level. The results provide insights into the mechanical response of the rocks, aiding in evaluating CO₂ utilization on stimulation and geo-storage applications which support sustainability. The following conclusions were drawn:

1. After 7 days, the nanoindentation displacement increased by 14.1% compared to the initial 460 nm. The shale rock deformed noticeably, with a 33.2% increase in displacement at day 30. Extending the analysis to 60 days, the displacement reached 44.7%, indicating continuous deformation.
2. After 30 to 60 days of sc-CO₂ exposure, long cracks formed on the shale surface, and holes and deposits were observed in SEM surface images. This phenomenon confirmed the reduced material strength.
3. Building upon these findings, future studies should explore the interplay between water and sc-CO₂ in influencing shale's mechanical integrity. It is also recommended to investigate shale interactions with other gases such as hydrogen.

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Vitae

Name	: [Dandi Alvayed]
Nationality	: [Indonesia]
Date of Birth	: [12 Februari 1999]
Email	: [dandialvayed@gmail.com]
Address	: [Permata Safir Rd No 88, South Jakarta 12210, Indonesia]
Academic Background	: [Master of Science in Petroleum Engineering]
Publication	: [Probabilistic estimation of hydraulic fracture half-lengths: validating the Gaussian pressure-transient method with the traditional rate transient analysis method (Wolfcamp case study). Journal of Petroleum Exploration and Production Technology, 1–16. https://doi.org/10.1007/S13202-023-01680-9] [The effect of the heavyweight hematite, magnetite, and micromax on class g oil well cement properties. Presented at the 57th U.S. Rock Mechanics/Geomechanics Symposium, Atlanta, Georgia, USA, June 2023. https://doi.org/10.56952/ARMA-2023-0490]