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Characterization of meso-scale mechanical properties of Longmaxi shale using grid microindentation experiments

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Abstract: Mechanical properties, such as the hardness $H$, Young’s modulus $E$, creep modulus $C$, and fracture toughness $K_c$, are essential parameters in the design of hydraulic fracturing systems for prospective shale gas formations. In this study, a practical methodology is presented for obtaining these properties through microindentation experiments combined with qualitative observations of the mineralogical phases using X-ray diffraction (XRD), scanning electron microscopy (SEM) with backscattered electron (BSE) imaging, and energy-dispersive X-ray spectroscopy (EDS) analyses. We apply this method in the case of three types of Longmaxi shales with different mineralogies (i.e. carbonate-, clay-, and quartz-rich, respectively), which allows us to determine the characteristic indentation depth, $h_i = 8-10 \, \mu m$, beyond which the mechanical response of the carbonate-rich shale is homogeneous and independent of its complex heterogeneous microstructure. Moreover, exploiting the results of a large number of indentation tests, we demonstrate that the indentation modulus $M$ of the shale increases as a power-law of hardness $H$, and its creep modulus $C$ increases linearly with $H$. We also compute the fracture toughness $K_c$ from the indentation data by assuming a perfectly plastic behavior of the sample. Our results are in good agreement with independent measurements of $K_c$ determined by microscratch tests. Finally, further tests on quartz- and clay-rich samples of the Longmaxi shale suggest further variations in the samples’ mechanical properties depending on their burial conditions and the mechanical properties of their dominant mineral phases.

Keywords: grid microindentation; mineral identification; hardness; modulus; creep; fracture toughness

1. Introduction

Shale is a multi-phase, multi-scale, compositionally diverse sedimentary rock composed of clay particles and silt-sized inclusions. It is often classified as an ultra-tight rock with relatively low porosity and permeability (Amann-Hildenbrand et al., 2012; Sakhaee-Pour and Bryant, 2012; Zhang et al., 2015b, 2017). In order to achieve economical and commercially viable gas production from shale formations, large-scale drilling and fracturing are necessary to generate complex fracture networks. One of the most challenging tasks is the accurate measurement/interpretation of the rock’s mechanical and mineralogical properties affecting the fracturing design process (Vernik and Milovac, 2011; Sone and Zoback, 2013a). Among the critical mechanical properties are (i) the fracture toughness $K_c$ that controls crack propagation (Mullen and Endler, 2012; Tarasov and Potvin, 2013); (ii) Young’s modulus $E$, which is a key parameter affecting fracture aperture in the process of hydraulic fracturing (Economides and Nolte, 2000; Smith and Montgomery, 2015); (iii) the hardness $H$ that influences proppant embedment and hence affects the ultimate fracture conductivity (Aramahi and Sundberg, 2012); and (iv) the creep modulus $C$, which is critical for understanding long-term reservoir completion and gas production (Li and Ghassemi, 2012; Sone and Zoback, 2013b; Rassouli and Zoback, 2015). The mineral composition itself is critical for evaluating the fracability of the formation (Rickman et al., 2008) and potential degradation caused by shale-fluid reaction (Du et al., 2018). Moreover, the volume fractions of the constituent phases are essential for estimating the strength of shale, while clay packing density has become a commonly used parameter to characterize the background clay matrix of shale (Ulm and Abousleiman, 2006; Ulm et al., 2007; Bobko and Ulm, 2008; Bobko et al., 2011).

Mechanical properties of rocks are usually obtained from conventional macroscopically homogeneous laboratory experiments. For instance, strength or stiffness can be measured from unconfined/confined triaxial (axisymmetric) compression/shear tests (Lama and Vutukuri, 1978), true triaxial shear tests (Colmenares and Zoback, 2002; Minaeian et al., 2014), or ultrasonic techniques (Wang, 2002; Dewhurst and Siggins, 2006). In the same vein, fracture toughness is determined from cracked chevron notched Brazilian disc (CCNBD), single edge notch beam (SENB), or three-point bending tests (Xiong et al., 2019; Zuo et al., 2019, 2020). These tests require relatively large samples and the results often suffer from high inter-sample variability. Besides, it is often difficult to obtain complete cores and perform logging from horizontal sections of the wellbore due to shale’s unstable structure and physicochemical properties (Wang et al., 2012, 2013; Ma and Chen, 2014).

In contrast, indentation methods first proposed by Oliver and Pharr (1992, 2004) have been developed to study the local mechanical properties of composite materials, such as ceramics, polymers, and geomaterials. Indentation tests consist in loading a material gradually up to a maximum force before releasing the applied load at the same rate. By controlling the indentation depth, the operator fixes the scale over which the mechanical properties (e.g. $H$, the indentation modulus $M$, and $C$) are determined. These methods allow estimating the mechanical properties in situations when it is challenging to extract intact core samples (using existing technologies). For example, microindentation tests have been conducted on small samples such as drill cuttings for studies of wellbore stability, drilling optimization, or refinement in the interpretation of seismic properties data (Chateau and Dormieux, 2002; Dormieux et al., 2002; Constantinides et al., 2006; Ortega et al., 2007). However, there is no standardization of microindentation tests for materials such as shale with complex microstructure to date. For instance, critical experimental parameters such as the characteristic indentation depth beyond which shale response is homogeneous, and the method for analyzing the mechanical properties obtained from massive indentation datasets, should still be addressed.

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Here we tackle these problems in the case of Longmaxi shales. The Silurian Longmaxi formation in Sichuan Basin, China, has recently been characterized as the primary target for shale gas exploration and development due to its high total organic content (TOC) value, favorable types of organic matter, high vitrinite reflectance ($R_o = 1.8\%$-$4.2\%$) values, abundant brittle minerals (average 56.3%), and strong gas generation intensity (Dai et al., 2014). Given the significance of the mechanical and mineralogical characteristics in shale gas exploitation and the inherent difficulties with measurements using conventional tests, this paper presents the results of a comprehensive mechanical and mineralogical characterization on samples of Longmaxi shale. We investigate the Longmaxi samples using a combination of massive grid nano- and micro-indentation, X-ray diffraction (XRD), scanning electron microscopy (SEM) with backscattered electron (BSE) imaging, and energy-dispersive X-ray spectroscopy (EDS) (SEM/BSE-EDS) techniques. Our observations allow us to determine a characteristic indentation depth beyond which shale properties are homogeneous (i.e. independent of the mineral phases’ actual spatial distribution). Moreover, we investigate how the mechanical properties of the Longmaxi shale vary across multiple samples of similar mineralogy and between samples with diverse mineral contents (carbonate- vs. silica- vs. clay-rich). Our results show that grid microindentation can provide a comprehensive assessment of essential mechanical properties for hydraulic fracturing design in prospective shale formations.

2. Materials and methods

2.1. Materials

Three different samples of the Longmaxi shale are considered in this study. Samples #1 and #3 are from shale outcrops, while sample #2 is from a borehole at a depth of ~3000 m. Under the optical microscope, the samples do not show any visible bedding planes. TOC contents of the samples were measured according to ASTM D2974-14 (2014) and are reported in Table 1. The shale samples were ground into powder using the McCrone Micronising Mill before being oven-dried at a temperature of 105 °C for 12 h to determine their water contents, which were 0.67%, 1.9%, and 0.54% for samples #1, #2, and #3, respectively. Then, the samples were incinerated at 440 °C for 12 h in a Thermo Scientific incinerator to remove the organic matter. This high-temperature incineration caused a notable change in the powdered samples’ coloration from dark black to light gray. The quantitative mineralogy of the powdered samples was determined and summarized in Table 1. Sample #1 contains a high percentage of carbonate minerals (calcite and dolomite, 30%), while sample #2 contains the most clay (illite and chlorite, 50%), and sample #3 contains the highest proportion of silicate framework minerals (quartz and albite, 60%).

Table 1. Quantitative mineralogy, water content, and TOC for Longmaxi shale samples from three locations.

<table>
<thead>
<tr>
<th>Components</th>
<th>Mass fraction of shale samples (%)</th>
<th>#1 (carbonate-rich)</th>
<th>#2 (clay-rich)</th>
<th>#3 (silica-rich)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite (A)</td>
<td>-</td>
<td>-</td>
<td>11</td>
<td>16.1</td>
</tr>
<tr>
<td>Calcium (C)</td>
<td>5.4</td>
<td>2.3</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Dolomite (D)</td>
<td>22.5</td>
<td>1.6</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Pyrite (P)</td>
<td>3.3</td>
<td>2</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Quartz (Q)</td>
<td>35.8</td>
<td>36.2</td>
<td>41.5</td>
<td></td>
</tr>
<tr>
<td>Chlorite (Ch)</td>
<td>-</td>
<td>9.9</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Illite (I)</td>
<td>26.6</td>
<td>34.9</td>
<td>29.2</td>
<td></td>
</tr>
<tr>
<td>Water content</td>
<td>0.67</td>
<td>0.54</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>TOC</td>
<td>6.3</td>
<td>2.1</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Sample preparation

Surface preparation of heterogeneous materials (such as shale) for microindentation tests aims to achieve a flat surface while minimizing disturbance of the mineral/particle and pore structure. In practice, during an indentation test, the indentation depth, $h$, must always be larger than the surface roughness of the sample, $R_q$, with typically $h > 3R_q$ (Bhuiy and Biswas, 1999; Donnelly et al., 2006). The trimmed shale samples with dimensions of $2 \text{cm} \times 2 \text{cm} \times 1 \text{cm}$ (length x width x thickness) were dry-polished using a series of 6 Silicon Carbide papers of decreasing grit size (down to 0.25 μm), followed by hand-polishing using diamond paper (1 μm grit size). In between each polishing step, the specimens were ultrasonicated in n-decane solution (non-reactive with the shale minerals and organic matter) for 5 min to remove the dust and particles left on the surface and in the pore structure.

Fig. 1. Representative AFM map of a polished region of shale sample #1. The AFM image is a 30 μm by 30 μm area, and the measured surface roughness $R_a = 16$ nm.

Atomic force microscope (AFM) tests were carried out to assess the surface roughness of the polished samples (Fig. 1). The data were acquired using a wave-mode or ‘tapping’ scan (Simpson et al., 1999). For each scan, the resolution was 512 × 512 pixels at a scan rate of 1 Hz. The chosen measurement of roughness was a root-mean-squared (RMS) average of the topography of the surface, $R_q$, defined by

$$R_q = \sqrt{\frac{1}{N} \sum_{i=1}^{N} z_i^2}$$

(1)

where $N$ is the number of pixels in each scan edge, and $z_i$ is the height from the mean plane at position (i, j). Shale samples prepared with the same procedure showed RMS roughness $R_q = 15-50$ nm.

2.3. Instrumented grid indentation technique

A series of indentation tests distributed evenly on a square lattice, and thus referred to as ‘grid indentation’, was used to characterize the shale samples’ linear and nonlinear mechanical responses at sub-micrometer and micrometer length scales. The indentation tests were carried out using a Micro/Nanotest indenter (Anton Paar, Graz, Austria). The Microtest and Nanotest platform can apply loads ranging between 0.03 N and 30 N with a resolution of 0.3 mN, and 0.1 mN to 500 mN with a resolution of 0.04 mN, respectively. The maximum measurable displacement (i.e. indentation depth) is 200 μm with a resolution of 0.3 nm and 200 μm with a resolution of 0.04 nm, respectively.
A grid of indentation tests was carried out on the polished surface of each sample. Calibrations of shape area function, electronic-mechanical interface, frame compliance, and thermal drift were checked before the indentation test (standard calibration procedures recommended by prior research are summarized in Appendix A).

Each test consists in indenting the shale’s surface with a Berkovich tip of half-angle of 70.32° and a curvature radius of approximately 30 nm. As illustrated in Fig. 2a, data collection follows a prescribed load function with the parameters listed in Table 2. The load is ramped up at a constant rate up to a maximum force, which is then maintained during 180 s (holding phase) to allow the sample to creep before unloading at a constant rate identical to that of the loading phase. The spacing between indentation points in each microindentation and nanoindentation grid is 300 μm and 10 μm, respectively (this separation ensures no interaction between the indents). Each microindentation and nanoindentation grid comprises 225 indents (square grid of 15 × 15 indents) and covers an area of 17.6 mm², and 441 indents (square grid of 21 × 21 indents) and covers an area of 0.04 mm², respectively. Moreover, the force-depth data of the grid microindentation test are processed to correct for contact point detection and exclude a small number of abnormal curves (caused by roughness issues, generation of indentation cracks, etc.) before computing the mechanical parameters.

Table 2. Testing parameters for microindentation experiments.

<table>
<thead>
<tr>
<th>Testing parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microindentation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loading rate</td>
<td>N/min</td>
<td>15</td>
</tr>
<tr>
<td>Unloading rate</td>
<td>N/min</td>
<td>15</td>
</tr>
<tr>
<td>Holding time</td>
<td>s</td>
<td>180</td>
</tr>
<tr>
<td>Approach speed</td>
<td>μm/min</td>
<td>16.6</td>
</tr>
<tr>
<td>Grid spacing</td>
<td>μm</td>
<td>300</td>
</tr>
<tr>
<td>Nanoindentation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loading rate</td>
<td>N/min</td>
<td>15</td>
</tr>
<tr>
<td>Unloading rate</td>
<td>N/min</td>
<td>15</td>
</tr>
<tr>
<td>Holding time</td>
<td>s</td>
<td>180</td>
</tr>
<tr>
<td>Approach speed</td>
<td>μm/min</td>
<td>2</td>
</tr>
<tr>
<td>Grid spacing</td>
<td>μm</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 2. Indentation loading function (a) and typical response (b). In (a), A, B, and C are the loading, holding, and unloading branches, respectively (b) shows the load vs. depth relation and key measures for determining the sample mechanical properties: the initial unloading slope, S, the maximum indentation depth, h_max, the residual indentation depth, h, the maximum force, F_max, the irreversible energy, U_irr, the plastic energy, U_pl, the fracture energy, U_f, and the elastic energy, U_e.

Determination of Young’s modulus, E, is based on the slope of the unloading curve. Upon unloading, the elastic energy stored in the material bulk during loading is recovered. Assuming a purely elastic unloading behavior, a straightforward dimensional analysis of the involved quantities yields the Bulychev-Alekhin-Shoroshorov (BASH) equation (Bulychev et al., 1975):

\[
\frac{1}{M_0} = \frac{1 - \nu^2}{E} + \frac{1 - \nu^2}{E_i}
\]

where \( M_0 \) is the reduced or indentation modulus, which reflects the comprehensive elastic response of the indenter and sample. For rigid indentation of an isotropic material, \( M_0 \) coincides with the plane stress modulus:

\[
M_0 = E \left[ \frac{1}{E_i} + \frac{1}{E} \right]
\]

where \( \nu \) is the Poisson’s ratio of the sample (here \( \nu = 0.2 \)) (Randall et al., 2000; Luo et al., 2020), \( \nu_i \) is the Poisson’s ratio of the diamond indenter (\( \nu_i = 0.07 \)), and \( E_i \) is the Young’s modulus of the diamond indenter (\( E_i = 1140 \) GPa). The following equation then allows calculating Young’s modulus:

\[
E = \left(1 - \nu^2\right)\left(\frac{1}{M_0} - \frac{1 - \nu^2}{E_i}\right)
\]

We characterize the creep results using the compliance method of Vandamme and Ulm (2013). The loading protocol of a 180 s long dwell...
period allows the assessment of the contact creep compliance rate in terms of the indentation depth, \( h \), and the effective contact radius \( a_c \):

\[
L(t) = 2a_c h F_{\text{max}}
\]  

(9)

where the creep compliance, \( L(t) = 2a_c h F(t) F_{\text{max}} + \text{const.} \), can be calculated from the time-dependent indentation depth rate and the change in indentation depth \( \Delta h(t) = h(t) - h_0 \) in excess of the indentation depth \( h_0 \), which is the indentation depth upon loading to \( F_{\text{max}} \). The parameter \( a_c = \sqrt{A/M} \) is the radius of contact between the indenter probe and the indented surface upon unloading.

A least-square fitting of \( \Delta h(t) = [h(t) - h_0] \) demonstrates that indentation creep compliance increases as a logarithmic function of time, which translates into a rate, \( L(t) \propto t^{-1} \). The creep rate is thus governed by \( C \) (Eq. (10)), which has the same dimension as an elastic modulus and is termed contact creep modulus. Finally, we condense the pre-\( 1/h \) term of \( L(t) \) into the contact creep modulus:

\[
C = F_{\text{max}}/(2a_c a_1)
\]  

(10)

where \( a_1 \) is the parameter derived by fitting the hold phase depth \( \Delta h \) and time \( t \) with \( \Delta h(t) = x_1 \log(t) + \text{const.} \).

(4) Fracture toughness

Due to the inhomogeneous nature of the samples and the difficulty in measuring the crack length directly during the nanoindentation process, we estimate fracture toughness from the energy absorbed by radial cracks propagating from the indentation imprint in brittle materials:

\[
K_c = \sqrt{G/M}
\]  

(11)

where \( G \) is the energy release rate.

The relationship assumes that mechanical work done during the indentation process can be written as follows:

\[
W = W_{\text{irr}} + W_e = W_{\text{irr}} + W_1 + W_2
\]  

(12)

where \( W_{\text{irr}} \) is the irreversible work, including the plastic (\( W_p \)) and fracture (\( W_f \)) work. The total (\( W \)) and elastic- \( W_c \) work can be easily calculated by integrating the measured force-deformation response (see Fig. 2b). Thus, the key to the fracture toughness’s determination is to separate the fracture energy from the irreversible energy (red area in Fig. 2b). For elastic-perfectly plastic materials, the indentation loading curve of load-deformation response can be fitted with a quadratic function, i.e. \( F = c_1 h^2 \), where \( c_1 \) is a function of the material’s mechanical properties and indenter geometry. If there are no fractures formed during the initial part of loading, the corresponding part of the \( F-h \) experimental curve can be well fitted by the function of elastic-perfectly plastic material. The upper limit of the selected part should be small enough to ensure no cracks initiate and should be large enough to involve adequate data for fitting. Herein, we assume that the upper limit is 10% of \( F_{\text{max}} \). As shown in Fig. 3, deviations from the projected \( F-h \) curve can be associated with fracture generation. Hence, the critical energy release rate \( G_c \) can then be determined as

\[
G_c = \frac{W_{\text{irr}}}{2A} = \frac{W_1}{A}
\]  

(13)

where \( A \) is the maximum contact area calculated by substituting \( h_{\text{max}} \) into Eq. (3). This method assumes that the crack growth under loading is stable. Finally, the fracture toughness can be computed from the energy release rate and the reduced modulus using Eq. (11).

2.4. Fracture toughness from microscratch tests

We have performed independent fracture toughness measurements using microscratch tests, following Akono and Ulm (2011, 2014). This procedure consists in scratching the surface of a polished sample using a diamond Rockwell indenter with a conical tip that ends by a sphere of 200 \( \mu \)m in radius. The indenter is drawn across the sample surface under a progressively increasing vertical load at a constant speed. As the scratch probe penetrates the material, fracture surfaces are generated along the probe’s base and sides, releasing fracture energy. Table 3 lists the parameters used in the tests discussed in the study.

Table 3. Testing parameters for microscratch experiment using a diamond Rockwell indenter with a conical tip that ends by a sphere of 200 \( \mu \)m in radius.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical scratches</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scratch length</td>
<td>mm</td>
<td>3</td>
</tr>
<tr>
<td>Scratch speed</td>
<td>mm/min</td>
<td>3</td>
</tr>
<tr>
<td>Maximum load</td>
<td>N</td>
<td>100</td>
</tr>
<tr>
<td>Loading rate</td>
<td>N/min</td>
<td>99.5</td>
</tr>
<tr>
<td>Horizontal scratches</td>
<td></td>
<td>119.5</td>
</tr>
</tbody>
</table>

Fig. 3. Derivation of fracture energy from microindentation test. The area \( S_\text{CD} \) from the measured loading phase of indentation includes elastic, plastic, and fracture components, while \( S_\text{OCD} \) is the model behavior of an elastic-perfectly plastic material (fitted to the initial phase of indentation). The fracture energy \( U_{\text{frq}} \) is derived from \( S_\text{CD} - S_\text{OCD} \).

Fracture toughness is interpreted based on linear elastic fracture mechanics, where the fracture toughness, \( K_c \), is written by

\[ K_c = \frac{F_T}{2p d(d)} \]

(14)

where \( F_T \) is the horizontal force; \( p \) is the perimeter of the indenter; and \( A \) is the horizontal projected load-bearing contact area, all evaluated at the scratch depth \( d \) into the sample surface. The fracture toughness, \( K_c \), is calculated from the force-penetration depth data for \( d \geq 0.5 h_{\text{max}} \) (Akono et al., 2012).

2.5. In situ mineralogical identification technique

Energy dispersive spectroscopy (EDS) is a common type of electron probe microanalyzer (EPMA) technique used for elemental analysis and mineralogy identification. The technique utilizes the X-ray spectrum emitted from the incited solid specimen when bombarded with a beam of electrons to provide local chemical analysis. In EDS, the emitted X-rays are classified based on their energy, and the volume of material that is probed depends on the electron beam energy and material density. One of EDS’s most essential applications is elemental mapping, which provides the spatial distribution of elements of interest over a specific area by collecting X-ray energies of secondary electrons resulting from the interaction between an electron beam and a sample. The EPMA technique has been widely used in geology, for instance, in the investigation of grain size distributions of individual minerals and porosity (Dilks and Graham, 1985; Tovey and Krinsley, 1991; Tovey et al., 1992; Krinsley, 1998; McGee and Keil, 2001). In the present study, electron microscopy observations and EDS mapping were carried out using a Carl Zeiss
Merlin HR-SEM system (ZEISS AG, Jena, Germany) equipped with an electron backscatter diffraction (EBSD) analyzer, which also provided EDS for in situ mineralogical identification. This elemental analysis was performed with an accelerating voltage of 15 kV and a working distance of 10 mm.

Fig. 4 summarizes the procedure for mineral identification. First, in order to analyze the effect of mineralogy on the mechanical properties, the surface area corresponding to the microindentation grid was fixed and scanned under SEM imaging. Second, the EBSD analyzers were inserted to generate the BSE image and EDS map with a resolution of 800 × 1024 pixels. Third, through Matlab coding, the quantitative element information stored in each pixel (corresponding to the real size of 0.3 μm × 0.3 μm) was extracted, and the in situ mineralogy of the testing area was identified pixel by pixel based on the XRD results and the uniqueness of elemental chemical composition of each phase in the studied organic-rich shale samples. Finally, the physical and mineralogical parameters, e.g. spatial distribution and area fraction of each component phase, and the particle size distribution of the inclusive minerals, were obtained from the ‘digital mineral map’ generated by the in situ mineralogical identification technique. The detailed process of the in situ mineralogical identification is addressed with an example in Appendix B.

![Fig. 4. Procedure for in situ mineralogical identification and analysis.](image)

Table 4. Area fractions of mineral phases in carbonate-rich Longmaxi shale. Results were obtained from seven specimens of carbonate-rich Longmaxi shale. Areas 1 and 2 belonged to specimen M1 and were distant by a couple of millimeters. Areas 3-8 were measured on specimens M2-M7.

<table>
<thead>
<tr>
<th>Area No.</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Pyrite</th>
<th>Quartz</th>
<th>Illite</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>20.2</td>
<td>18.7</td>
<td>2.1</td>
<td>22.4</td>
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<td>1.8</td>
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<td>14.7</td>
<td>0.6</td>
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<td>22.4</td>
<td>2.3</td>
<td>23.9</td>
<td>23.1</td>
</tr>
<tr>
<td>Mean</td>
<td>20.8±2.7</td>
<td>21.3±5.3</td>
<td>1.7±0.5</td>
<td>24.4±7.4</td>
<td>21±3.8</td>
</tr>
</tbody>
</table>

Table 4. Area fractions of mineral phases in carbonate-rich Longmaxi shale. Results were obtained from seven specimens of carbonate-rich Longmaxi shale. Areas 1 and 2 belonged to specimen M1 and were distant by a couple of millimeters. Areas 3-8 were measured on specimens M2-M7.

The constituent phases’ volume fractions are closely linked to the macroscopic mechanical properties (Kuila et al., 2014; Abedi et al., 2016a). In the literature, the volume fractions of each mineral phase are usually indirectly inferred from the mass fractions obtained in XRD experiments with average densities reported independently (Chen et al., 2015; Abedi et al., 2016b). The current methodology enables direct in situ micro-scale identification of mineral phases. Table 4 summarizes the area fractions of 5 principal mineral phases found in 8 regions of interest tested on M1-M7 of sample 91. Carbonate minerals (calcite and dolomite) account for 42% of the total mineral phases. Results show that the measured area fraction of each mineral phase ranges with a tiny standard deviation (of about 0.5%-5%), indicating that, at the measurement scale of 240 μm × 300 μm, the in situ micro-scale identification method can avoid the effect of heterogeneous nature of shale material on the mineralogy, and obtain the quantitative mineralogy information of shale composite.

3. Results

3.1. Determination of characteristic length

Once the indentation depth is much larger than the characteristic size of the constituent phases, \( D \), of the heterogeneous material, i.e. \( h/D \gg 1 \), the indentation response corresponds to the spatially averaged response of the material (Constantinides et al., 2006; Randall et al., 2009). In contrast, if the penetration depth is much smaller than the constituent phases’ characteristic size, the indentation measurement extracts the mechanical properties of the individual phases that compose the material. Thus, before performing the grid indentation experiments on the samples, we need to determine the penetration depths to derive statistically homogeneous properties.

In order to determine the characteristic indentation depth beyond which the mechanical properties are perceived as homogenous, a set of indentation experiments with different levels of the maximum penetration force, \( F_{\text{max}} \), is performed. Fig. 5 summarizes the resulting distributions of hardness values (Eq. (2)) over five selected ranges of maximum penetration depth, \( h_m \), resulting from the preset constant maximum penetration force for each grid indentation measurement. For \( h_m \leq 2 \mu m \),
the grid indentation data show a complex distribution function reflecting the influence of the different constituent mineral phases in the shale sample. In contrast, hardness values determined at indentation depths $h_m = 8-10 \mu m$ and 16-18 $\mu m$ are well described by a single Gaussian distribution function (with a small difference in the mean hardness due to the higher sensitivity to the sample defects and cracks for increasing penetration depths). Based on these data, we use $h_m = 8-10 \mu m$ as the characteristic indentation depth for estimating the homogeneous properties of the current shale samples. Note that the same conclusion can be reached when examining Young’s modulus.

To further verify the characteristic indentation length identified in this study, SEM/BSE imaging was carried out to detect the occurrence of different mineral phases associated with each microindentation. At a characteristic indentation depth of 8-10 $\mu m$, the microindenter probe has a surface contact diameter of 45-56 $\mu m$, which is much larger than the particle size of the mineral phases, as shown in Fig. 6. Hence, the interaction volume of indentation is sufficient to cover all the constituent phases.

### 3.2. Mechanical properties of carbonate-rich Longmaxi shale

We have performed microindentation measurements over a square grid (15 × 15 = 225 indents covering an area of 4.2 mm × 4.2 mm) with a constant maximum penetration force of 2.5 N to reach the maximum penetration depth within the range of 8-10 $\mu m$. Herein, the goal is to investigate the homogeneous mechanical properties of carbonate-rich Longmaxi shale. To avoid individual variations between specimens and the effects of testing zone choice, grid microindentation measurements were conducted on seven specimens (M1-M7), which were extracted from a single large block of intact carbonate-rich Longmaxi shale. The mean value of all the seven measurements is used as the final homogeneous mechanical result.

(1) Hardness and Young’s modulus

Fig. 7a and b compares the hardness and Young’s modulus for the seven specimens of carbonate-rich Longmaxi shale. The mean hardness values (Fig. 7a) range from 1.09 GPa to 1.52 GPa, with much closer agreement among six of the seven specimens, with the mean $H$ of all the seven specimens of 1.22 GPa and the standard deviation of $\sigma = 0.14$ GPa. The Young’s modulus $E$ is computed from the initial linear part of the unloading curves (Fig. 2a), which are used to calculate contact stiffness, $S$ (using Eqs. (5), (6), and (8)). Fig. 7b shows that the $E$ value ranges from 35.7 GPa to 42.8 GPa with a mean value across all specimens, $E = 39.2$ GPa, and the standard deviation of $\sigma = 2.6$ GPa. This result is consistent with elastic stiffness properties reported from uniaxial compression tests on carbonate-rich Longmaxi shale, e.g. $E = 39-41$ GPa, as reported by Shi et al. (2019). The data show that Young’s modulus from grid microindentation experiments where the underlying mineral phases have been homogenized ($h_m \geq 8-10 \mu m$) can be reliably interpreted as the macroscopic values.

Fig. 5. Hardness determined by grid indentations at various penetration depths for carbonate-rich Longmaxi shale. Data are presented as raincloud plots (Allen et al., 2019) and allow identifying a critical indentation depth beyond which the sample properties are homogeneous. Raincloud plots make it possible to visualize in a compact fashion: jittered raw data (red dots) and the probability distribution (red area) together with essential statistical parameters such as the statistical mean (black dot shown at the bottom of the probability distribution), the median, upper and lower hinges (quartiles) and the extremes (upper quartile + 1.5IQR and lower quartile – 1.5IQR, where IQR is the rank of the interquartile). The probability distributions for homogeneous and heterogeneous measurements are fitted by a single Gaussian function and multi-Gaussian functions with the two parameters (expectation $\mu$ and standard deviation $\sigma$), respectively. The two-dimensional maps are the results of interpolation analysis showing the spatial distribution of the measured hardness across the testing area.
(2) Creep modulus

Following the loading step, the maximum force was held for 180 s to measure shale samples’ creep behavior. As shown in Fig. 8, the indenter’s depth measured during the holding phase increases logarithmically as a function of time, which is used to determine a creep rate $x$, from which the creep modulus $C$ is computed using Eq. (10). Fig. 7c summarizes the creep modulus for all seven specimens of the carbonate-rich Longmaxi shale. The mean $C$ value of all the seven specimens is 903.5 GPa, and the standard deviation $\sigma = 114.8$ GPa.

(3) Fracture toughness

Fig. 7d summarizes the fracture toughness derived from the energy release rate (Eq. (13)) and the indentation modulus (Eq. (11)) determined by microindentation. The results show that the fracture toughness of carbonate-rich Longmaxi shale specimens ranges from 4.47 MPa m$^{1/2}$ to 9.29 MPa m$^{1/2}$ with an average value of $K_c = 5.75$ MPa m$^{1/2}$ with the standard deviation $\sigma = 1.7$ MPa m$^{1/2}$.

The fracture toughness determined by independent micro-scratch tests is $K_c = 5.4 \pm 0.6$ MPa m$^{1/2}$ (Fig. 9), in good agreement with the values determined from the microindentation tests.
Fig. 7. (a) Hardness, (b) Young’s modulus, (c) creep modulus, and (d) fracture toughness from grid microindentation tests with a maximum penetration depth of 8-10 µm for seven specimens (M1-M7), which are extracted from one single large block of intact carbonate-rich Longmaxi shale. Data are presented as a raincloud plot. The probability distributions are fitted by a Gaussian function with two parameters (expectation $\mu$ and standard deviation $\sigma$).

Fig. 8. Depth increase $\Delta h$ during the creep phase vs. time in a semi-logarithmic plot. The fit allows us to estimate the creep rate, $x_1$. Data from specimen M5 of carbonate-rich Longmaxi shale sample.

3.3. Effect of mineralogical composition on mechanical properties

The mineral composition of shales is critical for evaluating the fracability of the formation. The composition is closely related to the mechanical properties of shale. Therefore, quantitative mineralogy information, such as volume fractions of the constituent phases, is essential for estimating the sample’s strength and determining the clay packing density. By applying the in situ mineralogical identification technique developed in this study, quantitative mineralogy information of shale composite is obtained by scanning and analyzing couples of different regions at a scale of 240 $\mu$m × 300 $\mu$m. Fig. 10 compares the mineral phase maps of the three samples. The carbonate-rich sample #1 contains a nearly 50% area fraction of calcite and dolomite, sample #2 is clay-rich (50% area fraction of Illite and chlorite), while sample #3 is quartz-rich (56% area fraction of quartz and albite).

Fig. 9. Normalized tangential force vs. indenter depth $d$ normalized by its radius $R$. At large enough depth, the normalized tangential force converges towards the fracture toughness. A total of six scratch tests are performed (three scratches along a first direction reported in (a) and three scratches along the perpendicular direction reported in (b)) with a scratch length of 3 mm, and a scratch speed of 3 mm/min. The maximum force is 100 N in (a) and 120 N in (b), while the loading rate is 99.5 N/min and 119.5 N/min, respectively. The values of fracture toughness derived in (a) and (b) are $4.78 \pm 0.82$ MPa·m$^{1/2}$ and $6.01 \pm 0.97$ MPa·m$^{1/2}$, respectively. The solid lines represent the mean value of $K_c$, and the dashed lines represent the standard deviations of the measured $K_c$. Experiments are performed on carbonate-rich Longmaxi shale sample M1.
We have performed a more limited set of grid microindentation tests on the two other Longmaxi shale samples, i.e. clay- and quartz-rich. The indentation tests are conducted with a maximum indentation depth of 8-10 μm to access the homogeneous mechanical properties of the Longmaxi shales. We discuss these new results in comparison with those of Section 3.2. Fig. 11 compares the mechanical properties (H, E, C, and Kc) determined from grid microindentation experiments on the three samples. Samples #2 and #3 have slightly higher average hardness than that of sample #1 (H = 1.63 GPa and 1.67 GPa vs. 1.2 GPa; Fig. 11a), while sample #2 has a notably higher Young's modulus (E = 50 GPa vs. 39 GPa and 41 GPa; Fig. 11b). This result may be related to the overburden conditions of the three Longmaxi shale samples. Indeed, sample #2 experienced a slighter degradation under the borehole condition, which is not the case for samples #1 and #3 under the outcrop condition. The fracture toughness is higher for the clay-rich sample (#2, Kc = 7.97 MPa m^{1/2} vs. 5.75 MPa m^{1/2} and 6.62 MPa m^{1/2}; Fig. 11d), while the quartz-rich sample (#3) has the highest creep modulus of the three samples (C = 1393 GPa vs. 890 GPa and 1165 GPa; Fig. 11c). These results may be explained by the higher ductility of clay minerals (#2) compared to quartz and albite (#3), dolomite, and calcite (#1) (Jin et al., 2014).
4. Discussion

On one hand, Bobko and Ulm (2008) reported the micro-scale mechanical properties ($H$ and $M$) of shales as functions of the packing density ($\phi = 1-\phi$, where $\phi$ is the porosity) for indentation tests typically performed to depths $h_c$, ranging between 0.1 $\mu$m and 2 $\mu$m. On the other hand, more recent studies by Abedi et al. (2016a) have correlated the indentation properties (at $h_c = 0.5$ $\mu$m) to heterogeneous mineral phases (identified from EDS at 2 $\mu$m scale). Both of these prior studies are strongly affected by the heterogeneities in the particulate structure of shales. The current study uses deeper indentation depths, $h_c = 8-10$ $\mu$m, to obtain mechanical properties representing the homogeneous response of Longmaxi shale (note that similar homogenization depths have been reported independently for this material by Luo et al. (2020)).

Fig. 12 correlates the hardness and indentation modulus obtained from grid microindentation experiments on Longmaxi shale samples. Abedi et al. (2016a) proposed a unique power-law relationship between $H$ and $M$ based on indentation data for the clay/kerogen-rich phase of five different shales (with exponent $m = 0.74$). The current indentation data of a homogeneous carbonate-rich Longmaxi shale are also well represented by a power-law relation (but with a lower exponent $m = 0.57$). There is a much larger scatter in the more limited datasets for quartz- and clay-rich samples and the data suggest that the dominant sample mineralogy strongly influences the relationship between $H$ and $M$.

Deformations measured during the holding stage of the micromechanisms experiments are well represented by a logarithmic function, which allows us to compute creep modulus $C$, in agreement with long-term secondary compression data for clays (Meseri and Castro, 1989). Slim et al. (2019) concluded that indentation hardness $H$ and creep modulus $C$ were in a linear scaling relationship defined by the initial packing density and secondary consolidation coefficient. Fig. 13 shows that there is a strong linear correlation between the indentation hardness, $H$, and creep modulus, $C$, for carbonate- and clay-rich Longmaxi shale specimens (Fig. 13a) and much weaker correlations with Young’s modulus (Fig. 13b) using linear or power-law functions after Vandamme and Ulm (2009). Plasticity is an irreversible deformation, often attributed to fracture and slippage behavior at the microstructural level. The linear correlation between the indentation hardness and creep modulus, but not with Young’s modulus, may suggest that creep is related to specific plastic deformation processes (e.g. particle sliding) associated with indentation.

The fracture toughness values of carbonate-rich Longmaxi shale obtained by the method proposed in our study agree with the results measured by microscratch tests on our carbonate-rich Longmaxi shale as well as other carbonate-rich shales from other formations. For instance, Kabir et al. (2017) measured a black shale from Niobrara formation (a carbonate-rich shale, with a weight percent of calcite 70%), and the measured fracture toughness is within the range of 4.9-5.3 MPa m$^{1/2}$, which is very close to our results of 5.75 ± 1.7 MPa m$^{1/2}$.

In prior studies, fracture toughness was measured through the equation derived by Cheng et al. (2002) to determine the fracture energy consumed in the indentation process:

$$U_{fr}=1-\frac{1+(\frac{h_c}{2C})^{1/2}}{1-\frac{h_c}{4C}}$$

where $U_{fr}$ is the plastic energy, $U_t$ is the total energy, and $h_c$ is the residual indentation depth (see Fig. 2b). This method has produced highly accurate values.
variable estimations for Longmaxi shale from $K_c = 2-3.4$ MPa m$^{1/2}$ (Shi et al., 2019) to $K_c = 10.6$ MPa m$^{1/2}$ (Su et al., 2019). However, Eq. (15) was derived, assuming that the indentation curves were the response of ideal elasto-plastic material and that no cracks were generated during the indentation process. Hence, Eq. (15) may not be suitable for calculation of the fracture toughness.

Conventional macroscopic experiments on Longmaxi shale typically report lower fracture toughness (Xiong et al., 2019; Zuo et al., 2020) and are undoubtedly related to scale effects. The characteristic indentation depth determined in this study corresponds to the critical indentation response volume involving all the shale components, beyond which the elasto-plastic response is homogeneous. However, for the measurement of fracture toughness, the scale effects of cracks initiated and propagated should be considered as well. This result suggests that more experimental research is needed to understand the scaling effects on the fracture toughness in heterogeneous porous materials such as shales.

5. Conclusions

As a multi-phase, multi-scale, and highly heterogeneous composite material, measurements of shale’s mechanical properties are very sensitive to indentation depth. We use a statistical interpretation of the data in combination with mineralogical information obtained from XRD and SEM/BSE-EDS methods. It shows that a characteristic penetration depth, $h_t = 8-10$ μm, is required for the indentation hardness of Longmaxi shale to be represented by a single homogenized mineral phase.

We conducted an extensive set of these microindentations to characterize the indentation hardness, elastic modulus, creep modulus, and fracture toughness of homogenized, carbonate-rich Longmaxi shale. This material can be well characterized by a power-law relationship between $M$ and $H$, and a linear relationship between $C$ and $H$, which suggests that creep rates reflect viscoplastic deformation processes associated with indentation. The fracture toughness is interpreted by assuming a perfectly plastic behavior and estimated from work done in fracturing. A good agreement was found between microindentation estimates of $K_c$ and values obtained independently by microscratch tests (on Longmaxi shale and other carbonate-rich shales) (after Akono and Ulm, 2011, 2014). The fracture toughness values of Longmaxi shale measured by conventional macroscopic experiments are typically lower than our results, which should be attributed to the scale effects on fracture toughness measurement.

We also investigated shale mineralogy’s effects on the same mechanical properties obtained by microindentation on specimens of clay- and quartz-rich Longmaxi shale. The results show that the relationship between indentation modulus and hardness does not consist in a robust power-fit correlation for clay- and quartz-rich Longmaxi shale samples, and the linear relationship between creep modulus and hardness is much weaker for the quartz-rich Longmaxi shale. These results indicate that the mineralogical diversity significantly impacts the relationship between stiffness, hardness, and viscous shale properties.

This paper illustrates a comprehensive testing and analysis system to characterize shale’s mechanical and mineralogical properties at micro-scale. This method has the advantages of high accuracy, easy specimen processing, and attractive cost, which makes it practical for investigating the essential engineering parameters for hydraulic fracturing design in prospective shale formations.

Declaration of competing interest

The authors wish to confirm that there are no known conflicts of interest associated with this publication, and there has been no significant financial support for this work that could have influenced its outcome.

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Fig. 13. Correlations between creep modulus $C$ and (a) hardness $H$ and (b) Young’s modulus $E$ for Longmaxi shale samples. In (a), the data from carbonate- and clay-rich shale samples are fitted by a linear fit, $C = 724 H$ with $R^2 = 0.64$ and $C = 704 H$ with $R^2 = 0.62$, respectively. In (b), the linear or power-function correlation between $C$ and $E$ is much weaker for both carbonate- and clay-rich shale samples, $C = 23.3 E$ with $R^2 = 0.16$ or $C = 6.9E^{0.35}$ with $R^2 = 0.38$, and $C = 24.5 E$ with $R^2 = 0.35$ or $C = 0.077E^{0.45}$ with $R^2 = 0.36$, respectively.
experiments. The support provided by the China Scholarship Council (CSC) during a visit of Jiunting Du to MIT is acknowledged.

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Appendix A. Standard calibration procedures before indentation test

To ensure the accuracy of the measurement results, several calibrations were performed before the grid microindentation test (Deirieh, 2012).

(1) Shape area function

As introduced in Section 2.3, the projected area of contact \( A_s \) is a critical parameter for calculating the mechanical properties of the tested material. However, due to the bluntness of the Berkovich indenter, the area function \( A_s(h_c) \) needs to be calibrated. Typically, \( A_s(h_c) \) is calibrated by performing indentation tests on a calibration material with known mechanical properties (e.g. fused silica, whose indentation modulus is \( M = 72 \) GPa). Then, the contact depth \( h_c \) can be determined by the Oliver and Pharr method (Eq. (4)) and the projected area of contact \( A_s \) by the Bulychev-Alekhin-Shoroshorov (BASh) formula (Eq. (6)). The area function \( A_s(h_c) \) can then be fitted according to the measured \( h_c \) and \( A_s \) values of the calibration material:

\[
A_s(h_c) = C_1 h_c^2 + C_2 h_c + C_3 h_c^{1/2} + C_4 h_c^{1/4} + \ldots \quad (A1)
\]

where \( C_i \) is usually determined by the area-to-depth constant of the perfectly sharp indenter (e.g. for a Berkovich indenter, \( C_1 = 24.58 \)), and \( C_i \) (for \( i > 1 \)) is the factor influenced by the bluntness of the indenter.

(2) Electronic-mechanical interface

The interface between electronic and mechanical parts of the indentation apparatus, especially the relations of load-current and depth-capacitance, must be calibrated. The indentation load is applied electromagnetically by passing a current through a loading coil, and the indentation displacement is measured by the change in voltage of a parallel plate capacitor. Thus, the proportionality factor of relations of load-current and depth-capacitance must be calibrated every two years. The relation of load-current can be calibrated by hanging weights with a known mass on the indenter and then measuring the necessary current for drawing back the indenter to its initial position. The relation of depth-capacitance can be calibrated by performing indentation tests on a calibrated piezoelectric crystal with a spherical indenter.

(3) Frame compliance

In the process of indentation test, the frame of the indentation apparatus deforms simultaneously when applying a load to the sample. Thus, the recorded indentation depth \( h_{rec} \) actually consists of the real indentation depth in the sample (\( h \)) and the deformation of the apparatus frame (\( h_{frame} \)).

\[
h_{rec} = h + h_{frame} \quad (A2)
\]

The deformation of the frame \( h_{frame} \) can be determined by the frame compliance \( C_f \):

\[
h_{frame} = FC_f \quad (A3)
\]

where \( F \) is the load applied to the sample. The frame compliance \( C_f \) of the indenter is fixed as 0.1 nm/mN due to its specific design. Thus, its frame compliance requires no calibration.

(4) Thermal drift

During an indentation test, the thermal expansion or contraction of the sample and indentation apparatus can result in the variation in the indentation depth measurements, which is called thermal drift. Thermal drift can be calibrated by analyzing the hold period set at the beginning or end of an indentation test. However, the indentation apparatus does not require a thermal drift correction due to its reference ring design. The movement of the reference ring stays the same as the thermal drift of the sample.

Appendix B. Detailed processes of the in situ mineralogical identification

After acquiring the distribution of each element from EDS measurement (step 4 in Fig. 4), the unique elements of each mineral phase are used for mineralogical identification (Fig. 10). For instance, iron and sulfur are used to identify pyrite (see Fig. B1). As shown in Fig. B2, if only high-intensity calcium and no other unique elements (i.e. magnesium, iron, sulfur, silicon, and aluminum) are detected in a pixel, this pixel will be identified as calcite phase. Whereas if both high-intensity calcium and magnesium are detected in a pixel, this pixel will be identified as a dolomite phase (see Fig. B3). Carbon and oxygen are not used as the unique elements to analyze the mineral phases due to their wide existence in most of the constituent phases in shale.

Following a similar analysis of unique elements, the mineral phases will be identified pixel by pixel, and finally, the ‘digital mineral map’ of the entire scanned area will be generated by the in situ mineralogical identification technique (see Fig. B4a). As shown in Fig. B4b, the BSE image of the target area’s microstructures is presented herein to validate the precision of the ‘digital mineral map’ generated by the in situ mineralogical identification technique developed in this study.
Fig. B1. Identification of pyrite according to iron and sulfur: (a) Distribution of elemental Fe obtained from EDS; (b) Map of pyrite phase generated by in situ mineralogical identification technique.

Fig. B2. Identification of calcite: (a) Distribution of elemental Ca obtained from EDS; (b) Map of calcite phase generated by in situ mineralogical identification technique.

Fig. B3. Identification of dolomite: (a) Distribution of elemental Mg obtained from EDS; (b) Map of dolomite phase generated by in situ mineralogical identification technique.
Fig. B4. (a) 'Digital mineral map' generated by the in situ mineralogical identification technique and (b) The BSE image of the microstructures of the target area. The particles of mineral phases with different gray scales in the BSE image are in excellent agreement with the identification results in the 'Digital mineral map'.
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Table 1. Quantitative mineralogy and TOC for Longma xi shale samples from 3 locations
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Table 2. Testing parameters for microindentation experiments.
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Table 3. Testing parameters for microscratch experiment using a Doamong Rockwell indenter with a conical tip that ends by a sphere of radius 200µm.
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<tr>
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<td>Area 3</td>
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<tr>
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<td>21.3±5.3</td>
<td>1.7±0.5</td>
<td>24.4±7.4</td>
<td>21.3±3.8</td>
</tr>
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Table 4. Area fractions (%) of mineral phases in carbonate-rich Longmaxi shale. Results were obtained from seven specimens of carbonate-rich Longmaxi shale. Area 1 and 2 belong to specimen M1 and are distant by a couple of millimeters. Area 3 - 8 were measured on specimens M2 - M7.
Highlights:

• Mechanical properties of shale are determined by statistical microindentation tests;
• A characteristic indentation depth beyond which shale response is homogeneous is identified;
• Fracture toughness is determined by microindentation, and validated by independent microscratch tests;
• Mineralogy is identified by the proposed in-situ mineralogical identification technique;
• Correlations among indentation modulus, creep modulus, and hardness are discussed.
Conflicts of interest

The authors wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.