



HAL
open science

Linking elastic properties of various carbonate rocks to their microstructure by coupling nanoindentation and SEM-EDS

Youssef Abdallah, Matthieu Vandamme, Camille Chateau, Denis Garnier, Isabelle Jolivet, Atef Onaisi, Dimitri Richard, Soroosh Zandi

► To cite this version:

Youssef Abdallah, Matthieu Vandamme, Camille Chateau, Denis Garnier, Isabelle Jolivet, et al.. Linking elastic properties of various carbonate rocks to their microstructure by coupling nanoindentation and SEM-EDS. *International Journal of Rock Mechanics and Mining Sciences*, 2023, 170, pp.105456. 10.1016/j.ijrmms.2023.105456 . hal-04165900

HAL Id: hal-04165900

<https://enpc.hal.science/hal-04165900>

Submitted on 19 Jul 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Linking Elastic Properties of Various Carbonate Rocks to their 2 Microstructure by Coupling Nanoindentation and SEM-EDS

3 Youssouf Abdallah^{a,1}, Matthieu Vandamme^a, Camille Chateau^{a,*}, Denis Garnier^a,
4 Isabelle Jolivet^{b,2}, Atef Onaisi^b, Dimitri Richard^{b,3} and Soroosh Zandi^c

5 ^aNavier, Ecole des Ponts, Univ Gustave Eiffel, CNRS, Marne-la-Vallée, France

6 ^bTotal, CSTJF, Pau, France

7 ^cCS GROUP, Pau, France

8 ARTICLE INFO

9 *Keywords:*


10 Carbonate Rocks
11 Elastic Properties
12 Nanoindentation
13 SEM-EDS Analyses
14 Homogenization.

10 ABSTRACT

11 Characterizing the elastic properties of carbonate rocks is a crucial parameter in geotechnical
12 and reservoir engineering. However, these natural materials exhibit a wide variety of
13 microstructures, even when they belong to the same facies, leading to a significant dispersion
14 of their elastic properties. We focus on six selected rocks, for which global porosity is shown
15 to be not the only factor controlling elasticity. This study aims to understand which additional
16 microstructural parameters impact the rocks' elastic properties by means of nanoindentation
17 coupled with microscopic observations and analyses. A complete procedure is developed
18 to combine nanoindentation measurements with Scanning Electron Microscopy (SEM) -
19 Energy Dispersive Spectroscopy (EDS) analyses to identify volume fractions and elastic
20 properties of the mineral phases in each rock. The macroscopic Young's moduli are estimated
21 using analytical homogenization and are finally compared with the values obtained from
22 macroscopic experiments. We find that the mineral composition and mechanical properties
23 are critical parameters involved in carbonate rocks' elastic behavior. However, while capturing
24 the overall trend, homogenization is found to overestimate Young's modulus. A discussion
25 on the possible impact of cracks and non-spherical pores is conducted to explain this
26 overestimation. Besides, microindentation tests are carried out to explore higher scales, which
27 remain too small, however, to characterize the macroscopic Young's modulus of carbonate
28 rocks.

29
30
31
32 *NOTICE: This is a post-peer-review, pre-copyedit version of an article published in Inter-*
33 *national Journal of Rock Mechanics & Mining Sciences 170 (2023). The final authenticated*
34 *version is available online at: <https://doi.org/10.1016/j.ijrmmms.2023.105456>.*

*Corresponding author

 camille.chateau@enpc.fr (C. Chateau)

ORCID(s):

¹Present address : Terrasol, Paris, France

²Present address : TotalEnergies, CSTJF, Pau, France

³Present address : CVA engineering, Pau, France

36 **List of Symbols**

E_{exp}	Macroscopic Young's modulus measured through mechanical tests
E_{ref}	Reference value for the Young's modulus
E^{MT}	Homogenized Young's modulus using Mori-Tanaka schemes
E_{SC}^{hom}	Homogenized Young's modulus using self-consistent schemes
E_{hom}^h	Homogenized Young's modulus calculated with a consideration of cracks in the dominant phase
E_{hom}^α	Homogenized Young's modulus calculated with a consideration of spheroidal shape of pores
E	Young's modulus
K	Bulk modulus
G	Shear modulus
ν	Poisson's ratio
n	Number of phases in the material
h	Penetration depth of the indenter
F	Force applied with the indenter
L	Linear dimension of the probed volume by indentation
M	Indentation modulus
H	Indentation hardness
S	Unloading stiffness
A_c	Projected contact area
R_a	Arithmetic roughness
R_q	Quadratic roughness
f_i	Volume fraction of the phase i
d	Distance of an imprint to the nearest interface
d_{th}	Threshold on the distance d
ϕ	Porosity volume fraction
ϕ_{macro}	Macroporosity volume fraction
ϕ_{micro}	Microporosity volume fraction
μ_X	Mean value of the quantity X
σ_X	Standard deviation of the quantity X
t	Thickness of an elliptic crack
w	Width of an elliptic crack
l	Length of an elliptic crack
η	Crack density parameter
N	Number of cracks per unit volume
A	Area of an elliptic crack
P	Perimeter of an elliptic crack
α	Aspect ratio of a spheroidal shape

38 **1. Introduction**

39 Sedimentary rocks, formed through diagenetic processes occurring after the deposition of sediments, cover around
 40 73% of the Earth's land surface¹, and consequently, constitute potential reservoirs for hydrocarbons, CO₂ storage,
 41 and geothermal energy^{2,3}. Carbonate rocks are amongst the most complex sedimentary rocks, as they exhibit a large
 42 variety of microstructural features due to the complexity of their diagenesis^{4,5}. According to Flügel⁶, carbonate
 43 rocks hold between 40% and 60% of oil and gas reserves worldwide. Hence, there is a need to characterize the
 44 mechanical behavior of carbonate rocks in reservoir engineering. In this study, we focus on the elastic behavior of
 45 carbonate rocks.

46 Several macroscopic experiments performed on samples of carbonate rocks having similar porosities have shown
 47 a wide dispersion of elastic modulus⁵, proving that the global porosity is not the only factor controlling the elastic
 48 behavior. Many additional microstructural features, such as the volumetric ratio of grains to matrix, the presence,
 49 and type of cementation, the pore types, and the mineral composition, may be involved in the dispersion of the

50 elastic properties^{5,7-9}. Consequently, the prediction of macroscopic elastic moduli of carbonate rocks from the
51 knowledge of its microstructure and of the mechanical properties of its various microscopic phases remains a
52 challenging task.

53 This study investigates the elastic properties of carbonate rocks having comparable porosities through experiments
54 performed at the microscopic scale to understand the dispersion of macroscopic Young's modulus in light of
55 the microstructural attributes. Several rocks, having comparable porosities but different macroscopic Young's
56 moduli, are considered here. Our study is composed of an experimental part followed by a modeling approach
57 based on the homogenization theory. The instrumented nanoindentation technique¹⁰, which allows characterizing
58 the localized mechanical properties of every single phase of a material at the microscale level, is used here.
59 This technique has been increasingly carried out on rocks in the last decade since macroscale laboratory tests
60 are not sufficient to investigate the impact of microstructure (see the review of Ma et al.¹¹ and the references
61 therein). However, few studies have been conducted on carbonate rocks with nanoindentation compared to other
62 types of rock. Nanoindentation has been used on carbonates to assess the heterogeneity of the microscopic
63 mechanical properties^{12,13} and to characterize the impact of chemical interactions with the pore fluid (i.e.,
64 water¹⁴, brine¹⁵, CO₂-saturated brine¹⁵, or supercritical CO₂¹⁶) on the matrix microscopic mechanical properties.
65 Nanoindentation measurements on carbonates have been upscaled to predict macroscopic stiffness, by using a
66 self-consistent scheme¹² or a lattice spring model¹⁷, with the predictions being compared with macroscopic
67 ultrasound measurements. All those nanoindentation studies on carbonates focused on one or two rocks. On
68 geomaterials or cement-based materials, or even on bones¹⁸, nanoindentation tests can be combined with several
69 techniques to identify the phases of the studied material, such as optical microscopy¹⁹, Scanning Electron
70 Microscopy (SEM)¹⁸, Energy Dispersive Spectroscopy (EDS)²⁰⁻³¹, Wave Dispersion Spectroscopy (WDS)³²,
71 X-Ray microtomography^{33,34}, confocal laser scanning microscopy³⁵ and other imaging techniques³⁶.

72 Several groups employed a combined use of nanoindentation and SEM-EDS or EDX on shales. Kumar et al.²⁴
73 used EDS mapping over the grid indentation and found a correlation between the elemental heterogeneity of
74 the scanned region and the spread in indentation results. Mason et al.²⁵ performed grids of indentation on
75 Marcellus shales with various lithofacies. They then observed each indent with SEM and SEM-EDS and determined
76 mineralogy at the location of the indent. They studied how the properties of the individual phases depend on the
77 lithofacies. Abedi et al.²¹ employed the combined use of nanoindentation and SEM-EDS to identify what indents
78 were performed on pure phases, mixtures, and close to interfaces, such that they could measure the properties of
79 the fundamental building blocks of the material; they found out that stiffness and hardness of clay/kerogen-rich
80 phases exhibit a unique scaling relation. Mashhadian et al.²² employed a combination of the two techniques to
81 obtain phase properties that they input into micromechanical models; they found results from the upscaling in
82 good agreement with macroscopic measurements. Veytskin et al.²³ coupled nanoindentation with both SEM-EDS
83 and SEM-WDS to study shales; they showed that the nano-mechanical properties and morphologies of the various
84 phases are distinct. More recently, Liu et al.²⁰ combined nanoindentation with SEM-EDS and XRD techniques to
85 obtain the mechanical properties of individual phases in four shales; they showed in particular that the properties
86 of these individual phases at the nanoscale are quite diverse.

87 For what concerns cement-based materials, one can also find several studies that combined nanoindentation
88 with SEM-EDS or EDX. From a combined application of nanoindentation and SEM-EDS to low water-to-cement
89 ratio cement pastes, Chen et al.²⁶ found evidence for the formation of nanocomposites of calcium silicate hydrates
90 (C-S-H) with nanoportlandite. Moser et al.²⁸ combined nanoindentation with SEM-EDS mapping to identify
91 indents performed on hydrates in ultra-high-performance concrete. Wilson et al.²⁷ also combined statistical
92 nanoindentation and SEM-EDS of cement pastes with large replacements of cement by natural pozzolan; they
93 showed that the replacement by natural pozzolan leads to a transformation of C-S-H into C-A-S-H (calcium
94 aluminate silicate hydrates) and to the consumption of portlandite. Sorelli et al.³⁰ combined nanoindentation
95 and SEM-EDS on cement paste to identify indents performed in pure phases and hence avoid the need for
96 deconvolution. Bu et al.³¹ used SEM-EDS to obtain the composition at the location of individual indents in cement
97 paste; they showed that portlandite increases both the indentation modulus and the contact creep modulus. Zhang
98 et al.²⁹ characterized slag rims in cement-slag systems by a combined use of nanoindentation and SEM-EDS.

99 In contrast, on carbonates, correlation of nanoindentation results with the local microstructure was performed
100 based on optical microscopy or SEM imaging and, for one limestone lithofacies in a Marcellus shale only, based
101 on SEM-EDS²⁵.

102 In the present study, the nanoindentation technique is coupled with Scanning Electron Microscopy (SEM) and
103 Energy Dispersive Spectroscopy (EDS) to characterize the microstructure of the rocks and identify the mineralogy
104 under the indentation sites. Once the indentation grids are carried out on a sample, SEM-EDS analyses are
105 performed in ex-situ conditions. A method to identify the imprints, whose size is small, in the microscope, has been
106 developed and is presented here. Each indentation test can be consequently attributed to the corresponding phase,
107 and the elastic properties of each phase are obtained. Besides, an EDS map is performed on each sample's whole
108 surface to evaluate the solid phases' volume fractions. In addition, Mercury Intrusion Porosimetry (MIP) tests are
109 carried out to assess the pore size distribution and evaluate the volume fractions of the porosity families. Based on
110 these observations, a simple multiscale scheme of the microstructure is proposed for each rock. Then, analytical
111 homogenization models are used to estimate the rocks' macroscopic Young's moduli from the heterogeneous local
112 moduli, the assessed volume fractions of the different phases constituting the rock, and the proposed microstructural
113 scheme. Finally, the estimated values of the macroscopic Young's modulus are compared to the measured ones from
114 macroscopic experiments.

115 To the light of the literature presented in the previous paragraphs, our study presents several aspects that
116 are original for carbonates: 1) use of SEM-EDS mapping in complement to nanoindentation testing to identify
117 the mineralogy at the indent location, 2) extensive use and discussion of micromechanical modeling to predict
118 macroscopic stiffness, 3) experimental study of a relatively large number of rocks (i.e., six rocks) of various
119 facieses and mineralogical compositions. 4) Also, our methodological developments regarding the combined use
120 of nanoindentation grids with SEM-EDS mapping make it possible to automatize the characterization of the
121 mineralogical composition at each indent location. 5) The adopted procedure will also serve to conduct a critical
122 analysis of the simple use of the deconvolution technique, usually applied when no imaging is performed³⁷. In
123 fact, the deconvolution technique is known to lack robustness, in particular on cement-based materials, in the sense
124 that the mechanical properties deconvoluted for each phase may depend on how the deconvolution procedure is
125 performed³⁸. In our present work, we aim at providing a critical analysis of the deconvolution procedure, but for
126 carbonate rocks. Finally, note that the Python codes relative to the current study are available for interested readers
127 in the link given at the end of this paper.

128 The current paper is organized into six sections, besides this introductory section. In Section 2, the material
129 is presented, as well as the experimental procedure. Then, the experimental results are given in Section 3.
130 Homogenization is performed in Section 4 to estimate the macroscopic Young's modulus. A discussion about
131 the impact of microstructural attributes and the experimentally studied scale on the macroscopic Young's modulus
132 estimation is conducted in Section 5, before giving the main conclusions in Section 6.

133 2. Materials and Methods

134 2.1. Macroscopic Properties

135 Six carbonate rocks, denominated from A to F, are considered in this study. The Young's modulus of each rock was
136 measured from triaxial experiments performed at room temperature on cylindrical samples with a 3.8 cm diameter
137 and a 7.6 cm height. The method for Young's modulus measurement, based on an internal standard from Total (now
138 TotalEnergies), was the following. Each sample was equipped with two axial strain gauges and two radial strain
139 gauges and placed in a triaxial cell, which makes it possible to independently control the axial confining stress, the
140 radial confining stress, and the pore pressure. The samples were saturated with brine. The confining stresses were
141 increased isotropically at a rate of 1 bar per minute, together with the pore pressure, up to values close to the in-situ
142 effective stress. During this increase, the difference between the stresses and the pore pressure was kept constant.
143 The samples were then sheared by compressing the sample axially at a rate of 0.01 mm/min. A range over which
144 the relationship between the axial stress and the axial strain was linear was observed for all samples. The Young's
145 modulus was calculated as the slope of this relationship. Besides, the global porosity of each rock was measured
146 using a helium pycnometer. Results are shown in Figure 1.

147 Although Young's modulus tends to decrease with increasing porosity, these results clearly show that global
148 porosity is not the only factor controlling the elastic behavior. Rocks A, B, and C have very close porosity fractions
149 (around 12%), but exhibit a great dispersion in their Young's moduli (up to a factor of 2.3), even though the first two
150 rocks belong to the same facies F1 (see Figure 1). In addition, although Rocks D and E both have porosity fractions

151 around 20%, the Young's modulus of Rock D is almost double than that of Rock E. Finally, Rock F belongs to the
 152 same facies as that of Rocks A, B, and E, but has the highest porosity fraction. However, its Young's modulus is
 153 comparable to that of Rock B and even higher than that of Rock E. Therefore, other parameters than the global
 154 porosity are involved in controlling their elastic behavior.

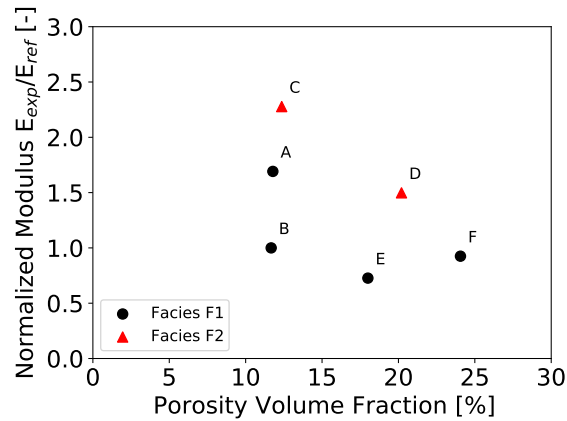


Figure 1: Facies and Young's modulus E_{exp} measured from macroscopic mechanical experiments and normalized by a reference value E_{ref} , plotted against the porosity volume fraction of several carbonate rocks.

2.2. Sample Preparation for Nanoindentation and Microscopy

155 The calculation of mechanical properties from the indentation response supposes that the sample surface is
 156 perfectly flat. Thus, the surface of the studied sample must be prepared cautiously to be as flat and smooth as
 157 possible. SEM-EDS observations also require small and smooth samples. Thus, a centimetric-scale piece of each
 158 rock was cut using a diamond wire. The samples were then coated with transparent resin (Epofix, Struers). The
 159 surfaces of the samples were polished using silicon carbide papers (SiC foil #220; #1200; #2000 and #4000,
 160 Struers) in dry conditions at first, and later, using MD-Dur discs made of woven silk (Struers) with 3- μm and
 161 1- μm alcohol-based diamond suspensions without the usage of a lubricant. The entire procedure can be found in
 162 the Ph.D. dissertation of Tazi³⁹.
 163

In order to provide meaningful results with indentation, the polished surface's roughness must respect a criterion defined in relation with the applied penetration depth of the indenter. The Atomic Force Microscopy (AFM) can be used to evaluate the roughness of a zone on the polished surface⁴⁰. This technique allows characterizing the surface's topography with high resolution, i.e., in the order of fractions of 1 nanometer. AFM characterization was performed on all the samples, and the quadratic roughnesses are found to take values between 21 and 28 nm over 40 \times 40 μm^2 sections. These values seem to be in line with those published in the literature^{39,41}. The Miller et al.⁴² criterion, proposed for cement paste materials, requires a quadratic roughness, evaluated on a square zone of side length l , such as:

$$\left(R_q^{l \times l}\right)_{l=200 \times \bar{h}} \leq \frac{\bar{h}}{5} \quad (1)$$

164 where \bar{h} is the mean penetration depth. For a bone material, Donnelly et al.⁴³ have found that the measurements
 165 of nanoindentation are not affected by the roughness when its value is lower than $\bar{h}/3$. In the absence of a criterion
 166 developed for rock materials (to our knowledge), the Miller et al.⁴² criterion is applied here on the 40 \times 40 μm^2
 167 sections and the following lower bound is obtained for the penetration depth: $\bar{h} > 5 \times 28 = 140$ nm.

2.3. Instrumented Nanoindentation Technique

2.3.1. Principles

168 The instrumented nanoindentation technique consists of pressing a hard diamond tip into the studied material⁴⁴.
 169 According to Larson et al.⁴⁵, the material domain in which the properties are measured has a characteristic linear

dimension L estimated at around ten times the penetration depth h for metals:

$$L \simeq 10 \times h \quad (2)$$

170 Whatever the factor is for rocks, shallower indentations identify the properties of a smaller volume of the material.
 171 Conversely, deeper indentations measure the properties of larger domains. The test comprises three phases: a
 172 loading phase followed by a holding phase and an unloading one. A visible imprint is left on the surface of the
 173 tested material's surface, with a dimension of about 5 to 6 times the maximum penetration depth. Two mechanical
 174 properties of the material are usually measured from the unloading curve:

1. The indentation modulus M (also called reduced modulus), which is defined as:

$$M = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_c}} \quad (3)$$

where $S = \left(\frac{dF}{dh} \right)_{h=h_{max}}$ is the unloading stiffness at the beginning of the unloading phase and A_c is the projected contact area at maximum depth. In the case of an ideally sharp Berkovich-type indenter, A_c can be related to the maximum depth h_{max} with the Oliver and Pharr⁴⁶ method as following: $A_c = 24.5 \times h_{max}^2$. The indentation modulus M is linked to the elastic properties of the indented material (Young's modulus E and Poisson's ratio ν) and of the indenter (E_i and ν_i) through the following relation:

$$\frac{1}{M} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (4)$$

2. The indentation hardness H , which represents the average pressure below the indenter, is defined as follows:

$$H = \frac{F_{max}}{A_c} \quad (5)$$

175 This parameter is often interpreted as a snapshot of the strength of the material^{47,48}.

176 In the present study, quasi-static indentation tests were performed using a NHT² nanoindentation tester from CSM
 177 Instruments (now Anton Paar) and a diamond Berkovich tip ($E_i = 1140$ GPa, $\nu_i = 0.07$). The tip imperfections
 178 were taken into consideration by calibrating the contact area A_c as a function of the penetration depth (using a
 179 fused silica sample and following the Oliver and Pharr⁴⁶ method). Grids of indentation tests were performed, as
 180 required to identify the properties of individual phases in heterogeneous materials such as rocks³⁷.

181 2.3.2. Nanoindentation Experiments

182 On each sample, four grids of 40 μm -spaced indentation tests were performed. The grids were carried out in a
 183 way to cover all the principal mineral phases of the studied material (preselected using SEM). Each grid is formed
 184 either by 20×20 or 15×15 tests, covering thus an area of $760 \times 760 \mu\text{m}^2$ or $560 \times 560 \mu\text{m}^2$, respectively. The
 185 maximum penetration depth was 200 nm, which respects the Miller et al.⁴² criterion (see Section 2.2), and is
 186 sufficiently small to obtain the individual properties of the phases. Each indentation test was performed with a
 187 loading/unloading rate of 6 mN/min and a holding duration of 10 seconds. All indentation curves were inspected
 188 visually, and those not sufficiently smooth were removed from the analysis.

189 To find the indented area in the SEM afterward (see Section 2.4), an artificial direct orthogonal frame was created
 190 with the indenter by performing three large imprints (up to the maximum force 500 mN) next to the sample's
 191 borders, as shown schematically in Figure 2a. The location of these tests was chosen to facilitate their identification
 192 in the SEM. In addition, to identify the position of each imprint of a grid accurately, this latter was performed with
 193 larger imprints at the four corners (see Figure 2b). The corner indentation tests were performed up to a maximum
 194 force of 40 mN, leaving imprints whose sizes are in the order of 6 μm .

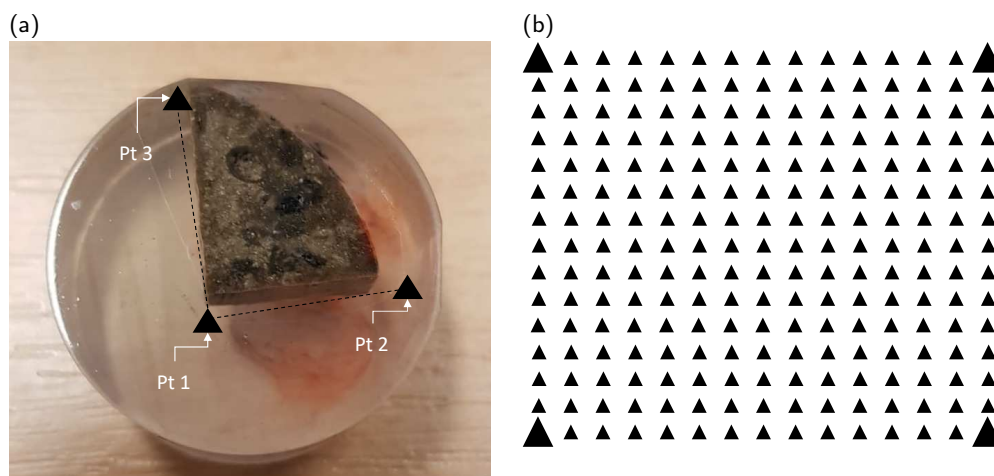


Figure 2: (a) Schematic of the direct orthogonal frame formed by 3 indentation tests performed on the sample; (b) Schematic of a typical indentation grid performed with large imprints at the corners.

2.4. Coupling Nanoindentation Measurements with SEM-EDS Mapping

2.4.1. SEM-EDS measurements

SEM-EDS observations were performed using a MEB-FEG Quanta 650 (FEI) microscope, with an acceleration tension of 15 kV. The minerals were obtained through QEMSCAN (Quantitative Evaluation of Minerals by Scanning Electron Microscopy) methodology, which is based on SEM-EDS elemental mapping. The SEM-EDS hypermaps are post-processed via the Nanomin Software (ThermoFisher), which compares the EDS spectra obtained on each pixel to a mineralogical database previously built according to the nature of the rock (carbonate, sandstone, etc.). The SEM-EDS QEMSCAN method has been shown to be an accurate quantitative tool to characterize mineralogy⁴⁹. The mineralogy of the studied facieses is simple, mainly composed of large grains of calcite and dolomite, and can be clearly identified using the QEMSCAN methodology.

Backscattered SEM images and EDS maps were performed on the zones covered by the indentation grids (see Section 2.4.2 below), with pixel sizes of 100 nm and 1 μm , respectively. The mineral composition of a layer whose thickness is 1 μm is rendered in the EDS maps. Therefore, the data of the latter maps roughly probe the same depth as indentation tests since the characteristic size of the indented domain was around 2 μm .

Finally, EDS mapping of the whole surface of the sample was also performed, with a pixel size of 20 μm , to get a statistically representative characterization of the mineralogical composition. A SEM image of the whole surface was also obtained in backscattered mode by stitching 16 images with a pixel size of 800 nm.

2.4.2. Identification of indentation locations in SEM-EDS images

After performing the indentation grids, each sample was inspected with SEM. However, it is complicated, if not impossible, to retrieve the indentation grids in SEM due to the indentations' small size. A two-step procedure was used to locate the indentation positions on the EDS maps, i.e. to identify the mineralogical phase located at each indentation test.

First, the grid's locations on the sample's surface were found based on the known coordinate systems of each experimental device. The coordinates of the three large imprints of the artificial frame defined in Section 2.3.2 (Figure 2a), easily recognizable in SEM images, were determined in the SEM coordinate system. A frame transformation, composed of a translation and a rotation, was then identified to convert the indenter to the SEM coordinate systems¹. This transformation was used to obtain the coordinates of the grids in the frame of the SEM from their known location in the frame of the indenter. Note that this simple geometric method here permitted

¹A Python script is written for this purpose. All the Python codes relative to the current study are available for interested readers in the link given at the end of this paper.

223 identifying indentation grid areas with an accuracy in the order of tens of micrometers. This is essentially due to
 224 the fact that the sample is not perfectly horizontal in the SEM.

225 Second, each indentation's location had to be inferred from the four deeper indentation locations at the corner of
 226 the grids. In fact, the imprints left by the 200 nm depth indentations were too small to be identified individually
 227 in the SEM. They could be mistaken for micropores or might not even be visible. On the contrary, the deeper
 228 indentations at the corners could be easily identified (Figure 3b). The global grid shapes were systematically found
 229 to be slightly deformed in the SEM images compared to the square shape performed in the indenter frame, as shown
 230 in Figure 3a. A 20×20 indentations grid, regularly spaced of $40 \mu\text{m}$ in the indenter frame, exhibits borders ranging
 231 from $760 \mu\text{m}$ to $764 \mu\text{m}$ (instead of $760 \mu\text{m}$) and angles varying between 89° and 91° . Therefore, a deformed
 232 grid had to be considered to predict all imprints' positions from the four corner positions. The deformation of the
 233 grid was assumed to be homogeneous. The mathematical developments of such geometric transformation can be
 234 found in Appendix A and were implemented in a Python script. Despite their shallow depth, some nanoindentation
 235 imprints could be retrieved in the SEM image presented in Figure 3a and were used to estimate this interpolation
 236 procedure's accuracy. Fifteen imprints were chosen randomly in the grid (in the central zone and around each
 237 corner), and the error between true imprints' positions and the interpolated ones were manually evaluated (e.g.,
 238 Figure 3c). The accuracy on the individual imprints positions is found to be lower than $3.5 \mu\text{m}$. The maximum
 239 error values were observed in the central part of the grid.

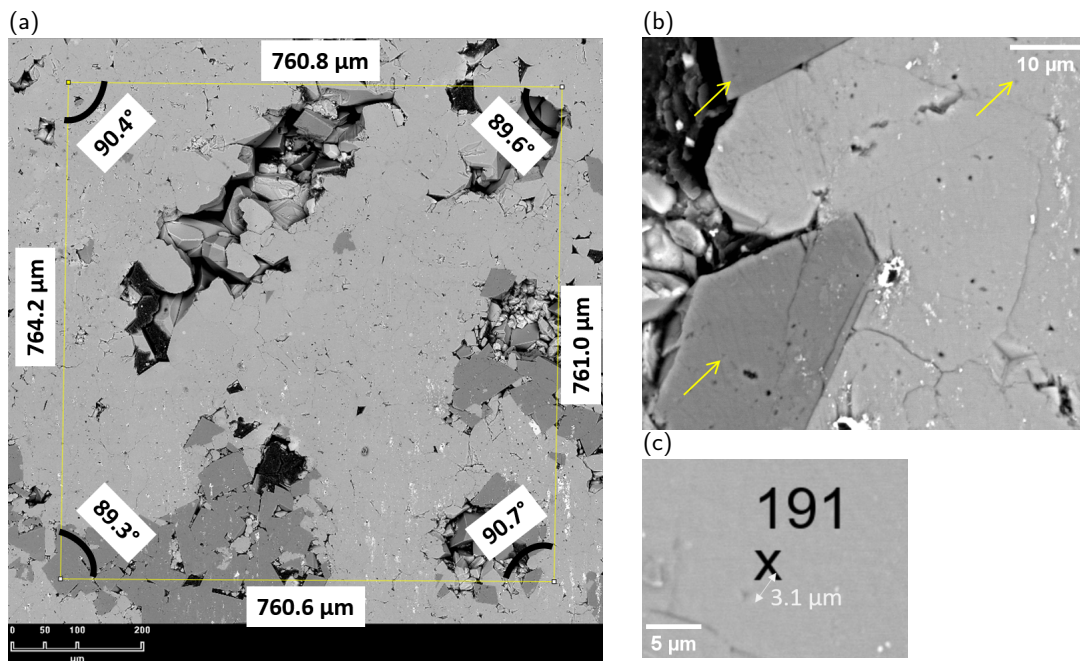


Figure 3: (a) SEM image showing the global geometry of an indentation grid of 20×20 tests regularly spaced of $40 \mu\text{m}$ in the indenter frame; (b) Enlargement in the lower right corner, showing the large corner imprint. The arrows point at the locations of the nearest 200 nm depth indentations. (c) SEM image showing the error between the real imprint position of the 191-th indentation of the grid and its position interpolated from those of the 4 deep corner imprints.

240 2.4.3. Exclusion of indentation tests near interfaces

241 Once the imprints' positions are found on the SEM and EDS maps, a phase can be attributed to each indentation
 242 test. However, to measure the properties of pure phases, the domain probed by an indentation test must be included
 243 entirely in a single phase. Therefore, the indentations whose probed volume would overlap two phases must be
 244 removed. The Euclidean distance d of each imprint to the nearest interface between two mineralogical phases
 245 has been automatically calculated after segmenting the EDS images (the whole procedure is available in Python
 246 language). Then, all the tests having a distance d lower than a threshold d_{th} have been excluded from the subsequent
 247 analysis. The value of d_{th} has been chosen to be greater than the sum of the maximum error on an imprint position

248 (3.5 μm) and the characteristic size of the probed domain by indentation (around 2 μm), leading to $d_{th} = 6 \mu\text{m}$.
 249 Notice that this method does not make it possible to remove indentations whose probed volume would overlap two
 250 phases if the second phase is right below the indented surface and not visible on the SEM-EDS images.

251 2.5. Typical Result

252 A typical result of a fully-studied indentation grid is presented in Figure 4. The grid, having a rectangular shape
 253 in the initial configuration (20 \times 10 indentations), covers a zone containing 3 phases. 87% of these 200 tests (i.e.,
 254 174 tests) were considered valid by the simple inspection of their force-penetration curves and retained in the
 255 subsequent procedure. The EDS map indicates that the matrix phase is formed with calcite, and many inclusions
 256 of dolomite and anhydrite phases are observed (dark grey and white color in the SEM image, respectively). The
 257 distance threshold has been applied to identify the indentations that would have probed a single phase, leading to
 258 a selection of only 87 tests, which are sorted by phase. Finally, the corresponding distributions of the indentation
 259 modulus M and hardness H are given in Figures 4c and 4d. For the various performed indentation grids, these
 260 histograms will be henceforth directly given for the sake of conciseness.

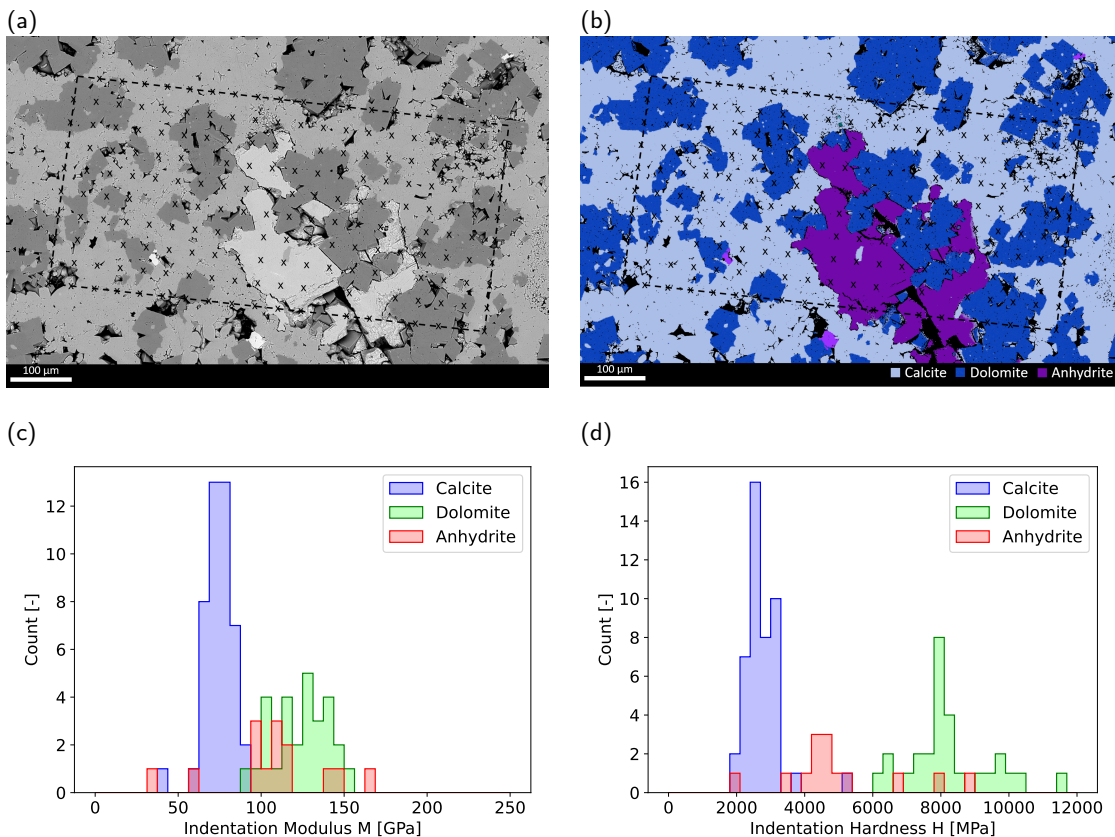


Figure 4: (a) Example of a SEM image over which the indentation grid is superimposed ; (b) Corresponding EDS map. Each cross stands for the location of one indentation test and the contour of the grid is marked here with dashed lines; (c)-(d) Histogram of the properties M and H of the identified phases: matrix of calcite with inclusions of dolomite and anhydrite.

261 3. Experimental Results

262 3.1. Microstructure's Characterization

263 As shown in Figure 5, a continuous calcite phase is identified in the rocks belonging to Facies F1: Rocks A,
 264 B, E, and F. Different mineral phases can be observed in this phase, such as dolomite and anhydrite (Rocks A

Table 1

Volume fractions of the rocks' phases evaluated from the EDS maps performed on the whole surfaces, and porosities measured from MIP tests. The mineral fractions are expressed with respect to the total volume. All values are rounded to 0.1%.

Rock	Calcite	Dolomite	Anhydrite	Quartz	ϕ_{macro}	ϕ_{micro}
Rock A	67.0%	19.9%	1.3%	0.0%	7.1%	4.7%
Rock B	70.5%	14.1%	3.7%	0.0%	5.8%	5.9%
Rock C	0.4%	72.6%	14.6%	0.0%	10.5%	1.9%
Rock D	0.0%	76.1%	3.7%	0.0%	13.3%	6.9%
Rock E	79.0%	0.0%	0.0%	3.0%	9.4%	8.6%
Rock F	74.1%	0.0%	0.0%	1.8%	N/A	N/A

265 and B), or quartz only (Rocks E and F). Figures 6, 7 and 8 present several SEM observations performed on the
 266 samples of Rock A to Rock F. In Rock A, large pores are observed at the millimeter scale, as well as isolated
 267 subspherical dolomite inclusions marked with the letter **D**. Besides, some anhydrite traces (marked by the letter **A**)
 268 are embedded in the calcite matrix. At lower scales, a family of micropores is observed in calcite (Figure 6d). In
 269 contrast, dolomite and anhydrite are quite more compact (Figures 6c and 6d). The diameters of micropores are at
 270 the scale of 1 μm , whereas macropores exhibit diameters ranging from several tens of micrometers up to the scale
 271 of 1 mm. As for Rock B, the dolomite phase seems to be less present and less homogeneously distributed in the
 272 volume space (Figure 5b) than in Rock A. The SEM observations on Rock B shown in Figures 6e and 6f suggest the
 273 presence of two porosity families again: micropores in the calcite phase and macropores at a larger scale. Anhydrite
 274 and dolomite seem to be quite compact. Besides, the SEM observations on Rock E and F presented in Figure 8
 275 make evidence of large subspherical macropores lying in the calcite matrix and a family of micropores at the scale
 276 of several micrometers. Minor traces of quartz are identified in the EDS maps performed on the whole surfaces of
 277 both Rocks E and F (Figures 5e and 5f).

278 On the other hand, Rocks C and D, which belong to Facies F2, exhibit a completely different microstructure
 279 (Figures 5c and 5d). Dolomite grains are found to form the major phase of these two rocks. In Rock C, subspherical
 280 grains of dolomite are identified (Figures 7a and 7b). An anhydrite cementation is found among the grains in some
 281 zones, and an intergranular porosity without evidence of cementation is observed in others. Unlike anhydrite, the
 282 dolomite phase is observed to contain a family of micropores. In addition, a small proportion of calcite is identified
 283 on the EDS map. However, the SEM observations performed on Rock D show the presence of angular crystals of
 284 dolomite (Figures 7c and 7d). Moreover, anhydrite is less present in this rock, as only minor isolated traces are
 285 identified. Besides, no calcite phase has been observed in the EDS map of this rock.

286 The mineral phases' surface fractions are evaluated from the EDS maps carried out on the samples' whole surfaces
 287 (Figure 5). These fractions are assumed here to be equivalent to the volume fractions with respect to the total volume
 288 (following Delesse⁵⁰). Since EDS probes only the solid skeleton, those volume fractions are measured with respect
 289 to the volume of the solid skeleton. We then multiply those volume fractions by $(1 - \phi)$ (where ϕ is the total volume
 290 fraction porosity assessed by MIP), to obtain mineral volume fractions expressed with respect to the total volume
 291 of the sample. Results are gathered in Table 1. Calcite forms the major phase in the rocks belonging to Facies F1,
 292 whereas dolomite is the major phase in the rocks of Facies F2. Between Rocks A and B, dolomite is more present in
 293 the former. Minor traces of anhydrite are identified in both rocks (less than 4%). In contrast, Rocks E and F exhibit
 294 only the minor presence of quartz inclusion. For Facies F2, anhydrite is more present in Rock C than in Rock D.
 295 No calcite is identified in Rock D, whereas only 0.4% of calcite is found in Rock C.

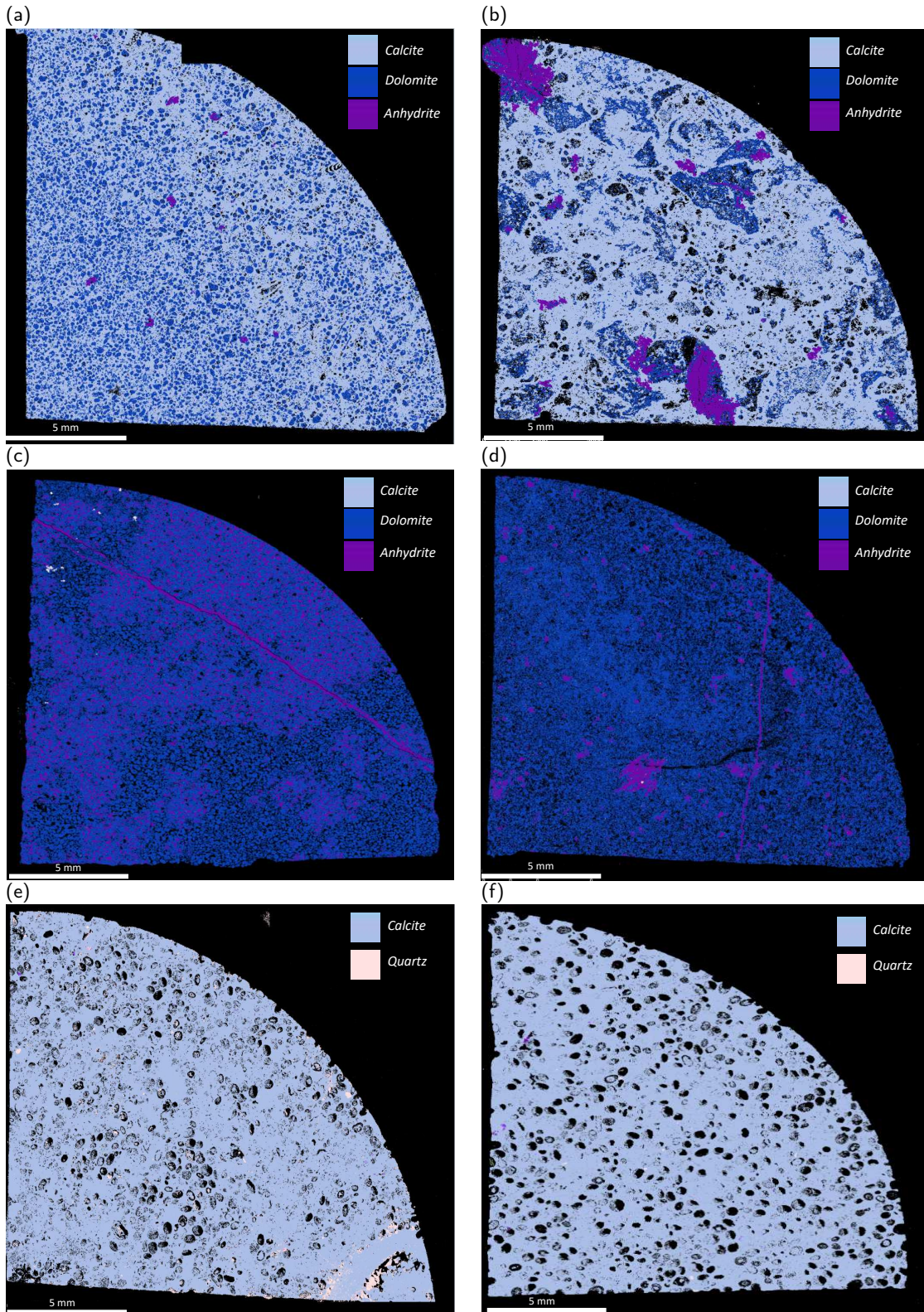


Figure 5: EDS maps performed on the whole surface of the samples: (a-f) Rocks A to F.

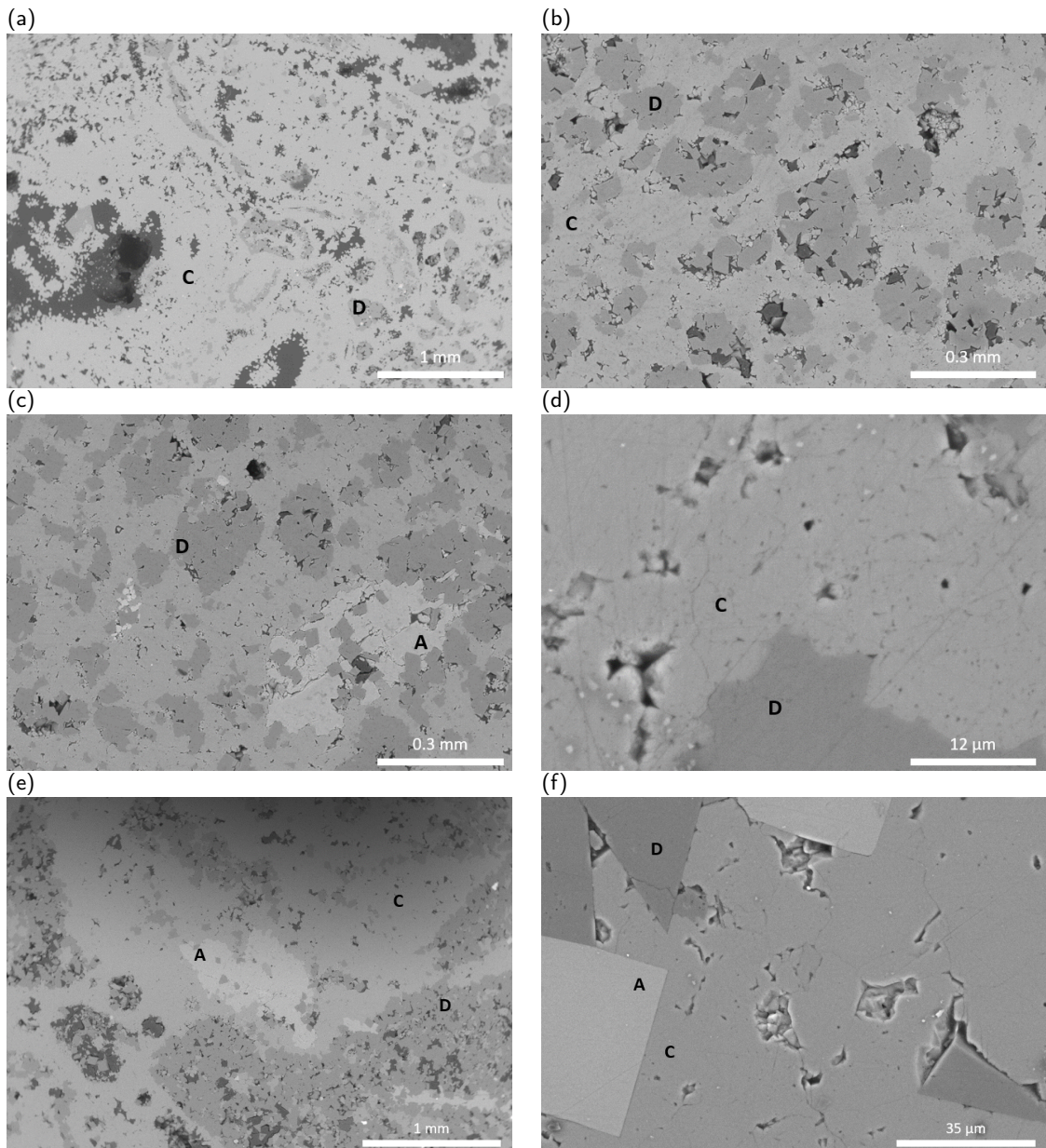


Figure 6: Backscattered SEM observations of: (a-d) Rock A; (e-f) Rock B. The letters C, D and A denote calcite, dolomite and anhydrite, respectively.

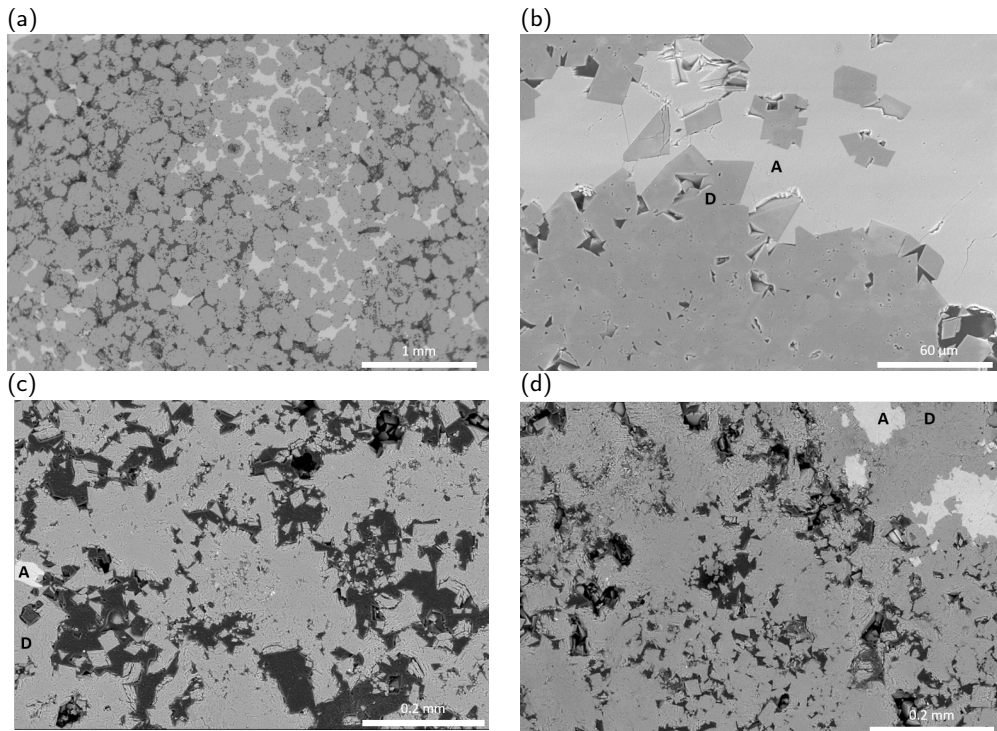


Figure 7: Backscattered SEM observations of: (a-b) Rock C; (c-d) Rock D. The letters D and A denote dolomite and anhydrite, respectively.

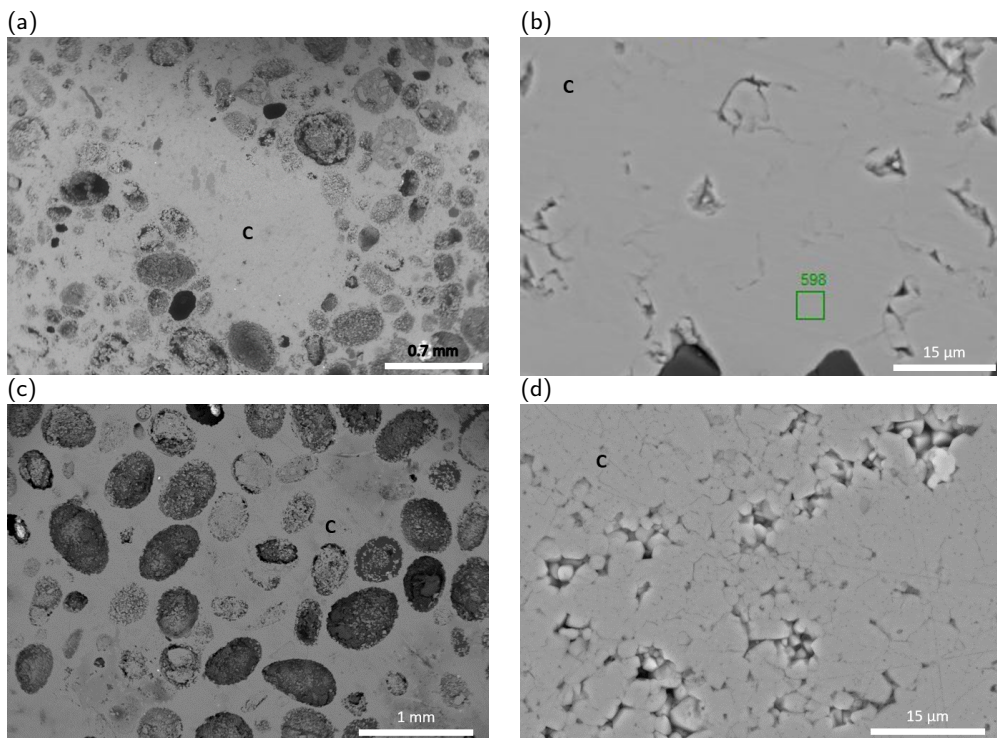


Figure 8: Backscattered SEM observations of: (a-b) Rock E; (c-d) Rock F. The letter C denotes calcite.

296 Moreover, MIP tests have been conducted on samples cored from Rocks A to E to evaluate the porosity
 297 families' volume fractions (Figure 9). Unfortunately, the sample of Rock F that we possess had been already
 298 tested mechanically (to measure its macroscopic Young's modulus), and its microstructure had been thus deformed.
 299 Therefore, MIP has not been performed on a sample from this rock. Note that the total porosities of the samples
 300 provided in Table 1 are close to the one displayed in Figure 1 and obtained by helium pycnometry on companion
 301 samples: this good agreement suggests that our samples are representative.

302 The MIP curves of Rocks A to C, which have global porosities around 12%, are gathered in Figure 9a. The
 303 dominant pore size is in the 10 μm range for Rocks A and C. We observe no clear peak for Rock B, whose pore
 304 size distribution extends from 0.1 to 10 μm . Figure 9b shows the MIP results corresponding to Rocks D and E,
 305 whose global porosities are between 18% and 20%. The MIP curves of Rock D and E exhibit peaks at 0.5 μm and 3
 306 μm , respectively. It is worth mentioning that at a given global porosity, the rock which contains more microporosity
 307 is the one whose Young's modulus is the lowest (Rock B in Figure 9a and Rock E in Figure 9b). This result is in
 308 agreement with the results published by Weger et al.⁷.

309 For modeling purposes, we will need the volume fraction of the various porosity families. Based on the
 310 microstructural observations and the MIP measurements presented above, we introduce a threshold diameter
 311 between microporosity and macroporosity and set it to 2 μm for all the studied rocks. Accordingly, the volume
 312 fractions of the porosity families are given in Table 1. The impact of the value of this threshold on the homogenized
 313 mechanical properties will be discussed in Section 4.3.

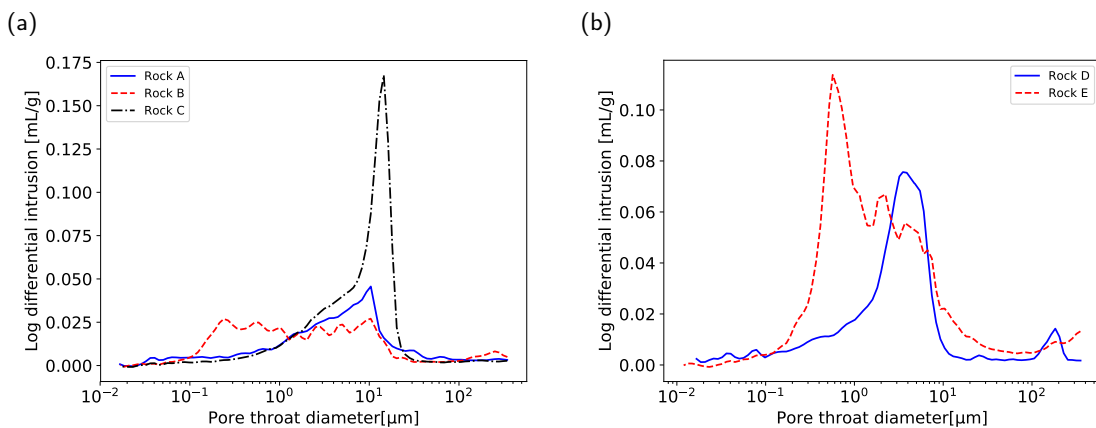


Figure 9: Results of MIP conducted on samples extracted from Rocks A to E.

Table 2

Mean values (μ_M and μ_H) and standard deviations (σ_M and σ_H) of, respectively, the indentation modulus and hardness obtained for the rocks' solid phases.

Rock	Calcite		Dolomite		Anhydrite	
	$\mu_M \pm \sigma_M$ [GPa]	$\mu_H \pm \sigma_H$ [GPa]	$\mu_M \pm \sigma_M$ [GPa]	$\mu_H \pm \sigma_H$ [GPa]	$\mu_M \pm \sigma_M$ [GPa]	$\mu_H \pm \sigma_H$ [GPa]
Rock A	75.1 ± 11.6	2.8 ± 0.6	125.5 ± 15.8	8.4 ± 1.2	107.1 ± 31.6	5.0 ± 1.7
Rock B	63.3 ± 17.8	2.4 ± 0.7	105.4 ± 24.0	5.7 ± 1.7	91.3 ± 24.0	3.4 ± 0.6
Rock C			130.6 ± 16.1	7.4 ± 1.1	108.5 ± 16.9	4.0 ± 0.7
Rock D			105.9 ± 15.7	5.1 ± 1.0		
Rock E	48.4 ± 11.6	1.7 ± 0.7				
Rock F	59.4 ± 10.7	1.7 ± 0.6				

3.2. Local Mechanical Properties

314
315 Nanoindentation experiments have been conducted following the procedure presented in Section 2. The corre-
316 sponding histograms of the indentation modulus M and hardness H classified by phases for Rocks A to C and
317 Rocks D to F are given in Figures 10 and 11, respectively. The mean values μ and standard deviations σ of the
318 indentation properties of the rocks' mineral phases are then calculated and listed in Table 2. Dolomite is found to
319 be the stiffest and hardest phase in comparison with calcite and anhydrite, as its indentation modulus's mean values
320 μ_M vary between 105.4 and 130.6 GPa and its indentation hardness's mean values μ_H vary between 5.1 and 8.4
321 GPa. Calcite is the softest phase, with $48.4 < \mu_M < 75.1$ GPa, and $1.7 < \mu_H < 2.8$ GPa. The properties of calcite
322 in Rock E are lower than in the rocks of Facies F1, which may explain its lower value of Young's modulus (Figure
323 1). Anhydrite has intermediate properties with $91.3 < \mu_M < 108.5$ GPa, and $3.4 < \mu_H < 5.0$ GPa. When a phase
324 is rarely present in the microstructure, its properties may sometimes not be measured from nanoindentation grids,
325 as is the case for calcite in Rock C, anhydrite in Rock D, and quartz in Rocks E and F. The obtained results are
326 consistent with those measured by Tazi³⁹, who has studied a source rock and obtained the following properties for
327 calcite: $70.1 < \mu_M < 73.0$ GPa and $\mu_H = 2.5$ GPa, and for dolomite: $97.0 < \mu_M < 107.0$ GPa and $5.8 < \mu_H < 6.4$
328 GPa.

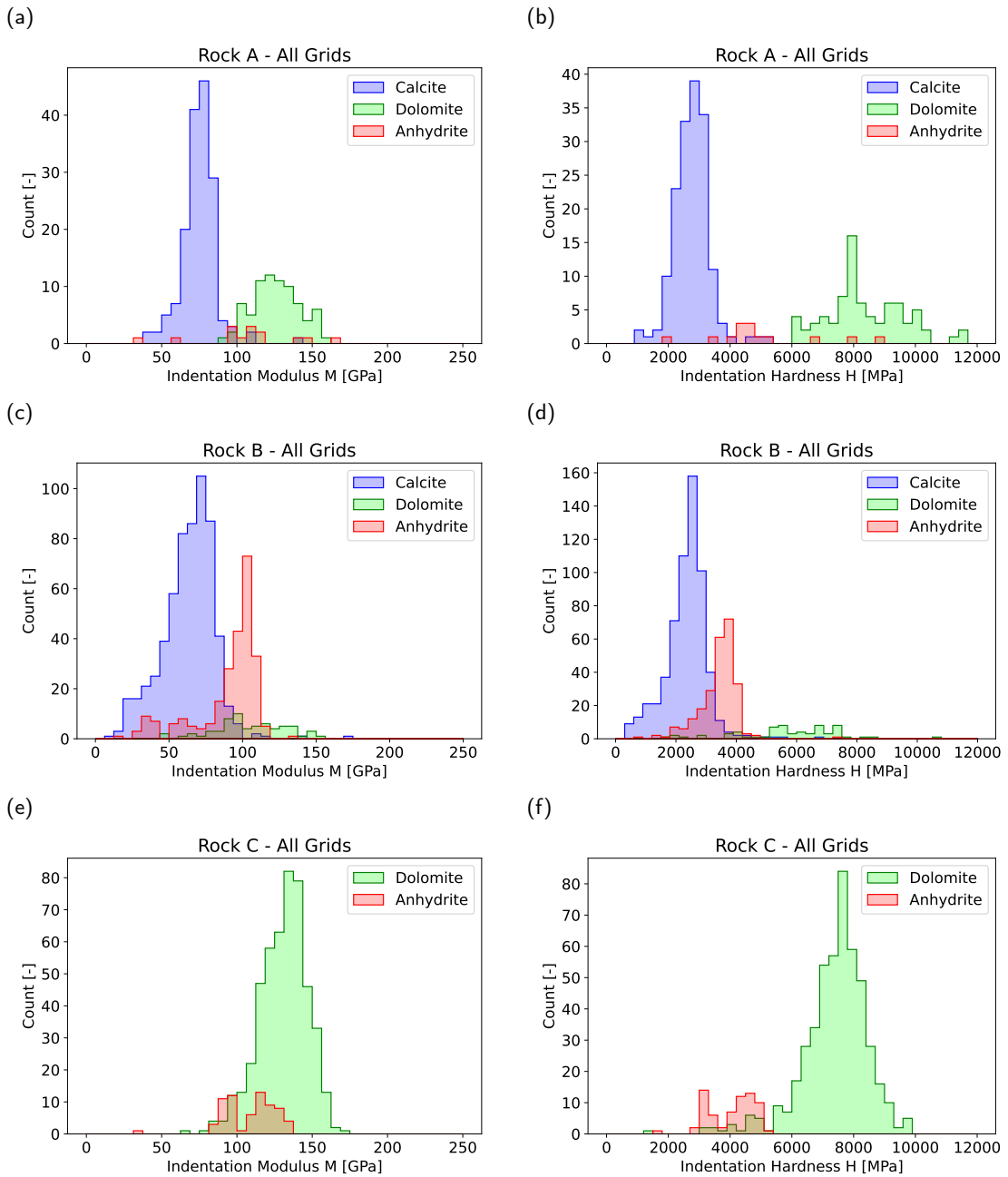


Figure 10: Histograms of the indentation modulus M and hardness H obtained from all the grids performed on the sample of (a)-(b) Rock A; (c)-(d) Rock B; (e)-(f) Rock C.

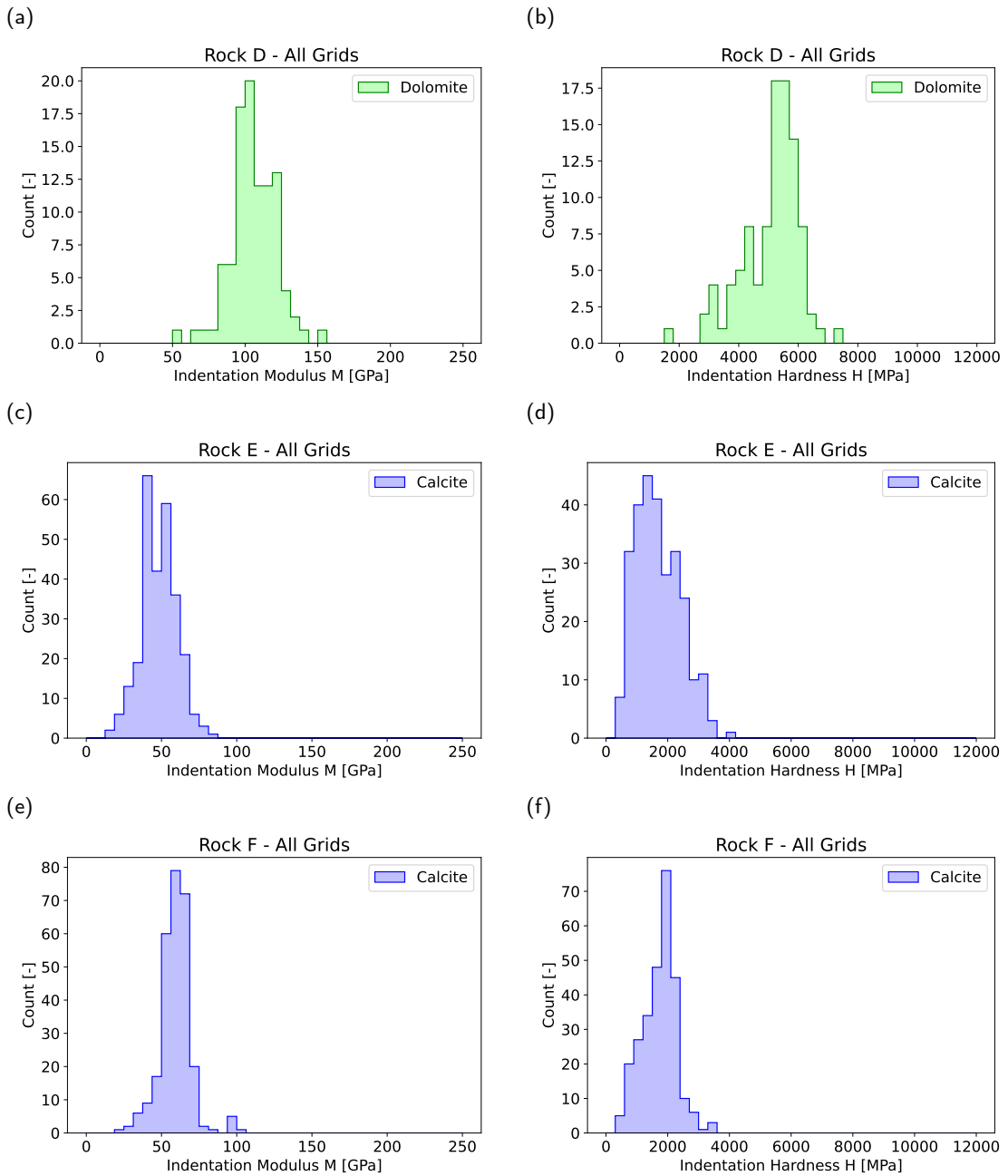


Figure 11: Histograms of the indentation modulus M and hardness H obtained from all the grids performed on the sample of (a)-(b) Rock D; (c)-(d) Rock E; (e)-(f) Rock F.

Table 3

Volume fractions (f_i), mean values (μ_M and μ_H) and standard deviations (σ_M and σ_H) of indentation modulus M and hardness H for each phase identified in all grids performed on rocks A, B and C, obtained from the SEM-EDS analysis (EDS) and from the deconvolution procedure (*dec*). Volume fractions are rounded to 0.1%. Volume fractions indicated for the SEM-EDS analysis are the fraction of indentation tests associated to each mineral as obtained from the combined procedure described in section 2.4 and shown in Figure 10.

Rock		Phase 1 - Calcite			Phase 2 - Anhydrite			Phase 3 - Dolomite		
		f_i [%]	$\mu_M \pm \sigma_M$ [GPa]	$\mu_H \pm \sigma_H$ [GPa]	f_i [%]	$\mu_M \pm \sigma_M$ [GPa]	$\mu_H \pm \sigma_H$ [GPa]	f_i [%]	$\mu_M \pm \sigma_M$ [GPa]	$\mu_H \pm \sigma_H$ [GPa]
A	EDS	64.0	75.1 ± 11.6	2.8 ± 0.6	5.5	107.1 ± 31.6	5.0 ± 1.7	30.4	125.5 ± 15.8	8.4 ± 1.2
	dec	53.2	70.9 ± 10.6	2.5 ± 0.7	16.9	97.9 ± 16.4	5.4 ± 1.2	29.9	130.6 ± 16.3	8.6 ± 1.8
B	EDS	65.9	63.3 ± 17.8	2.4 ± 0.7	27.1	91.3 ± 24.0	3.4 ± 0.6	7.0	105.4 ± 24.0	5.7 ± 1.7
	dec	88.0	66.5 ± 20.9	2.5 ± 0.7	9.6	104.7 ± 5.3	5.4 ± 1.2	2.4	140.1 ± 23.7	8.6 ± 1.8
C	EDS				12.4	108.5 ± 16.9	4.0 ± 0.7	87.6	130.6 ± 16.1	7.4 ± 1.1
	dec				38.2	101.1 ± 20.2	5.0 ± 1.4	61.8	134.4 ± 13.1	7.6 ± 0.7

3.3. Critical Analysis of the Deconvolution Technique

If no SEM-EDS mapping is performed after indentation, the deconvolution technique may be applied to estimate the mineral phases' volume fractions and their indentation properties. This paragraph is devoted to present a critical analysis of this technique in light of the results obtained from coupling nanoindentation and SEM-EDS imaging. The deconvolution technique is applied on the cumulative histograms of indentation modulus M and hardness H obtained for rocks A, B and C by following the deconvolution procedure of Ulm et al.¹⁰: we fit a normal distribution to each property of each phase, by preventing overlapping of the peaks. Therefore, 5 quantities are sought for each phase: its volume fraction f_i , the mean values μ_M and μ_H and the standard deviations σ_M and σ_H . The indentation tests considered for this technique are those selected after inspecting their force-penetration curves (i.e., the first stage of test selection presented in Section 2.3.2 prior to the MEB-EDS characterization). In each of the deconvolution analyses, the number of phases imposed corresponds to the one identified with SEM-EDS imaging, i.e. 3 and 2 phases for rocks A/B and rock C, respectively. For rocks A and B, the initial guess parameters of the minimization procedure were set to $\mu_M = (70, 100, 125)$ GPa and $\mu_H = (2.5, 6, 8)$ GPa for phases (1, 2, 3), respectively. For rock C, they were set to $\mu_M = (100, 125)$ GPa and $\mu_H = (5, 8)$ GPa for phases (1, 2). In all cases, a relative standard deviation of 0.3 has been considered for both M and H distributions, as well as equal volume fractions for all phases.

Figure 12 and Table 3 display the results obtained for the three rocks. The following conclusions can be made:

1. For the three rocks, although the orders are respected, most deconvoluted volume fractions differ from the ones estimated after SEM-EDS characterization.
2. Depending on the histograms, the deconvolution can lead to mean mechanical properties that differ significantly from the coupled approach using SEM-EDS characterization, i.e. up to 33% for the indentation modulus (rock B, dolomite) and up to 60% for the indentation hardness (rock B, anhydrite). In such cases, coupling SEM-EDS measurements with the nanoindentation data is required to obtain accurate measurements of the mechanical properties.

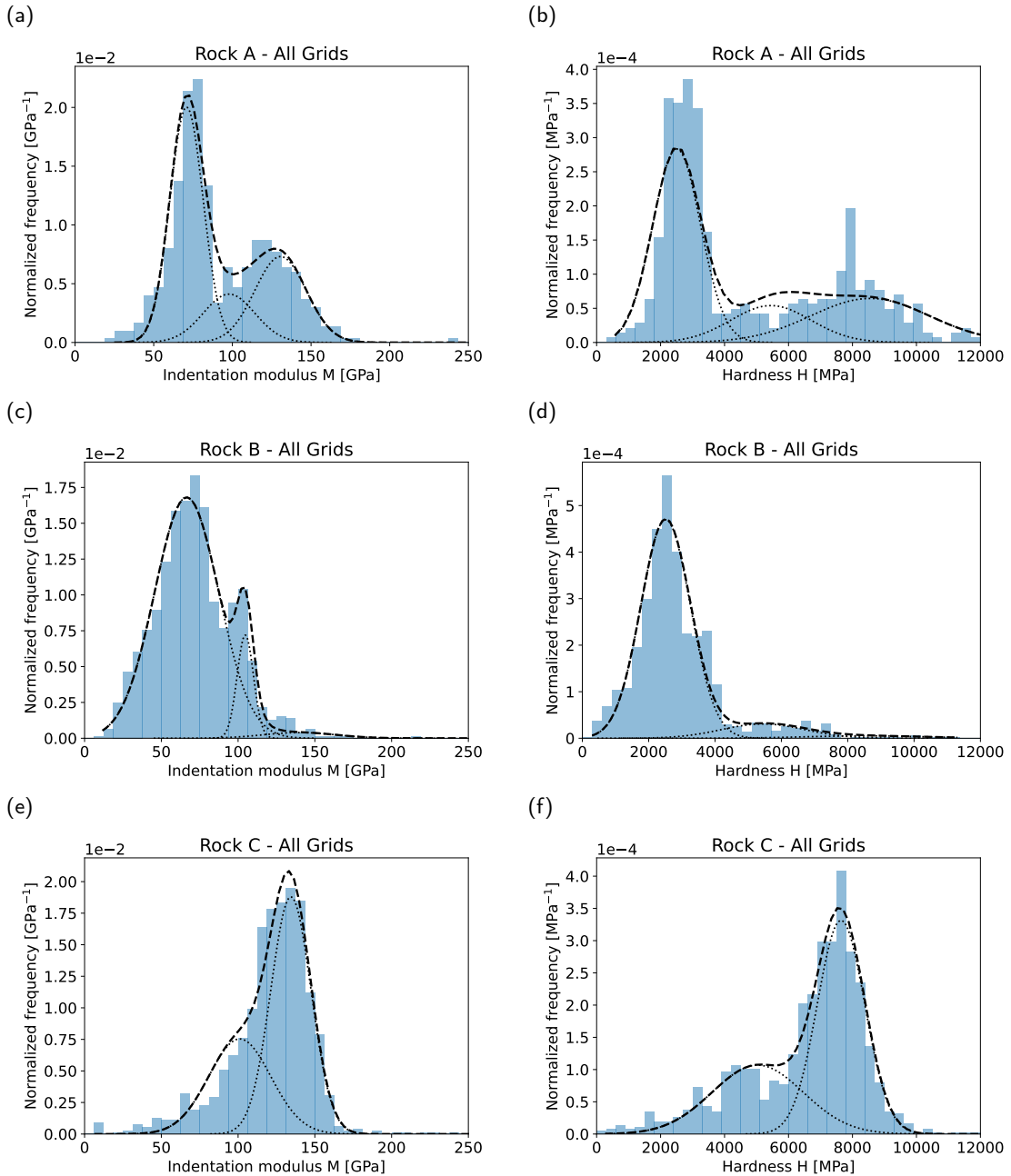


Figure 12: Histograms of indentation modulus M and hardness H for all grids performed on (a-b) Rock A, (c-d) Rock B and (e-f) Rock C, and corresponding analyses with the deconvolution method. The dashed lines represent the summation of normal distributions weighted by the volume fractions, and the dotted ones represent the individual phase distributions.

353 4. Homogenization of the Young's Moduli

354 The homogenization theory is applied on the experimental results presented in the previous section to estimate
355 the macroscopic values of Young's modulus of each rock.

356 4.1. Homogenization Principles

357 The homogenization theory consists of modeling a heterogeneous material with a homogeneous one, which
358 behaves globally in the same way⁵¹. In our case, we are interested in modeling the elastic behavior of rocks having
359 different microstructures with equivalent homogeneous media in terms of the bulk and shear moduli: K and G .
360 In this theory's frame, the homogenized elastic properties depend on each phase's elastic properties forming the
361 microstructure, their volume fractions, and morphologies. In the case of an Eshelbian type morphology⁵², where
362 the phases of the heterogeneous medium are assumed to have ellipsoidal shapes, two main schemes exist in the
363 literature:

- 364 1. The Mori-Tanaka scheme⁵³, where the main phase is assumed to form a continuous matrix in the material.
- 365 2. The self-consistent scheme⁵⁴, which corresponds to polycrystal materials, where none of the phases forms
366 a real continuous phase.

In the case of a Mori-Tanaka scheme, the homogenized bulk and shear moduli of a medium formed by a matrix
(index 1) and $n - 1$ phases (index 2 to n) with a spherical shape are respectively expressed as⁵¹:

$$K_{hom}^{MT} = \left(\sum_{j=1}^n \frac{K_j f_j}{1 + \alpha_1 \left(\frac{K_j}{K_1} - 1 \right)} \right) \left(\sum_{i=1}^n \frac{f_i}{1 + \alpha_1 \left(\frac{K_i}{K_1} - 1 \right)} \right)^{-1} \quad (6)$$

$$G_{hom}^{MT} = \left(\sum_{j=1}^n \frac{G_j f_j}{1 + \beta_1 \left(\frac{G_j}{G_1} - 1 \right)} \right) \left(\sum_{i=1}^n \frac{f_i}{1 + \beta_1 \left(\frac{G_i}{G_1} - 1 \right)} \right)^{-1} \quad (7)$$

where f_i , K_i and G_i represent the volume fraction, bulk and shear moduli of a phase i respectively, $\alpha_1 = 3K_1/(3K_1 + 4G_1)$, and $\beta_1 = 6(K_1 + 2G_1)/[5(3K_1 + 4G_1)]$. In this case, the index 1 refers to the matrix phase. As for the self-consistent scheme, the homogenized moduli for a n -phases material with spherical shapes have the following expressions⁵¹:

$$K_{hom}^{SC} = \sum_{i=1}^n \frac{K_i f_i}{1 + \alpha_{hom} \left(\frac{K_i}{K_{hom}^{SC}} - 1 \right)} \quad (8)$$

$$G_{hom}^{SC} = \sum_{i=1}^n \frac{G_i f_i}{1 + \beta_{hom} \left(\frac{G_i}{G_{hom}^{SC}} - 1 \right)} \quad (9)$$

367 with $\alpha_{hom} = 3K_{hom}^{SC}/(3K_{hom}^{SC} + 4G_{hom}^{SC})$ and $\beta_{hom} = 6(K_{hom}^{SC} + 2G_{hom}^{SC})/[5(3K_{hom}^{SC} + 4G_{hom}^{SC})]$.

368 The self-consistent indentation technique is an alternative approach proposed by Randall et al.⁵⁵ to estimate the
369 homogenized elastic properties of a material directly from a grid of indentation measurements without the need
370 of SEM-EDS analyses. This approach assumes that each indentation test is representative of a material phase, and
371 an equivalent "virtual" composite material, composed of n randomly and equivalently distributed phases, can be
372 defined. The number of phases n is identical here to the total number of indentation tests. In such a medium, none
373 of the phases can play a matrix's role, and thus, a polycrystal morphology seems to be well-suited. Therefore, we
374 adopt the self-consistent scheme to calculate the homogenized elastic moduli (Equations 8 and 9).

4.2. Homogenization Strategy Inferred From Observations

Based on the microscopic observations presented in Section 3.1, a two-scale scheme is proposed to describe the microstructure of the rocks belonging to Facies F1 and is illustrated in Figure 13a. At the largest scale, a continuous calcite phase containing dolomite, anhydrite, quartz, and macropores is assumed. At the lowest scale, microporous calcite is considered. Another two-scale scheme is proposed to describe the microstructure of the rocks belonging to Facies F2 and is illustrated in Figure 13b. At the largest scale, a dolomite phase containing anhydrite, calcite, and macropores is considered. At the lowest scale, dolomite is considered to be microporous. In-between micropores, both calcite and dolomite could contain nanopores at the scale below (i.e., less than 100 nm). Nanoindentation provides measurements that include the impact of those nanopores on the mechanical properties of the mineral phases. The MIP measurements show the volume of those nanopores to be negligible compared to the total pore volume (Figure 9).

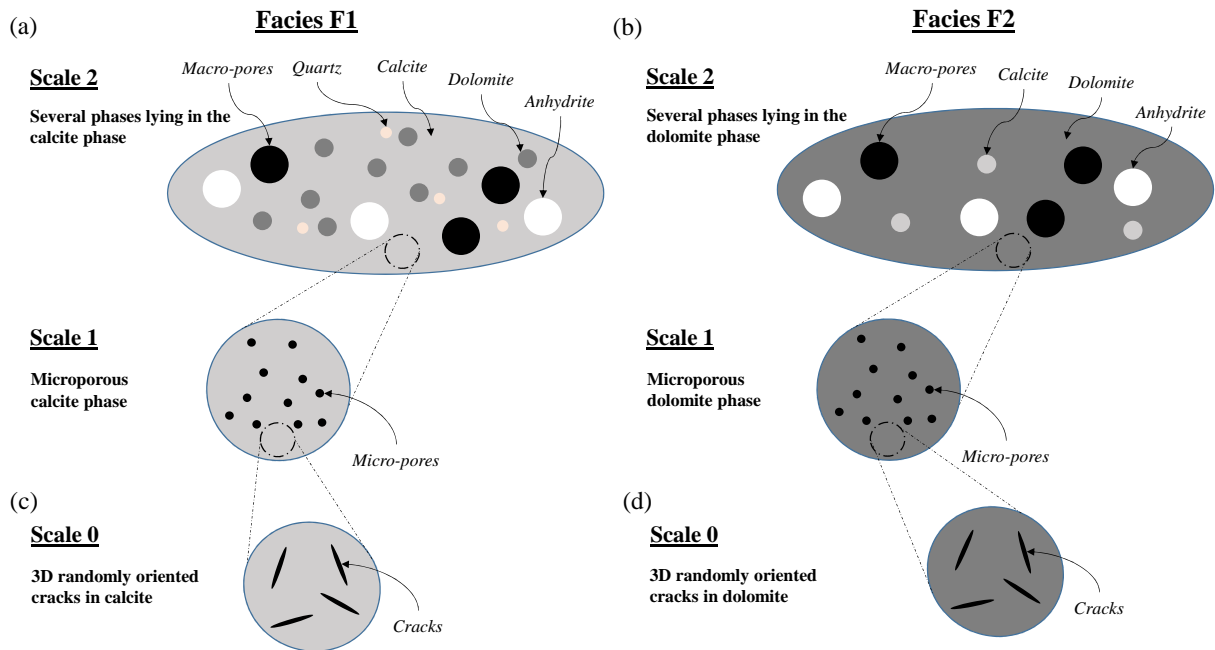


Figure 13: (a)-(b) Two-scale schemes proposed to describe the microstructures of the rocks belonging to Facies F1 and F2, respectively; (c)-(d) Additional lower scale introducing 3D-randomly oriented elliptic cracks in the dominant phase of the rocks belonging to Facies F1 and F2, respectively.

The homogenization technique is then applied on the two-scale schemes, taking into account the volume fractions of the different phases and porosity families given in Table 1, and their local properties presented in Table 2 (see also Equation 4). We consider a Poisson's ratio $\nu = 0.3$ for all minerals, except for quartz, for which $\nu = 0.08$ ⁵⁶. Finally, due to the lack of data on the following phases, some assumptions have been made:

- The properties of calcite in Rock C are taken identical to those obtained for Rock A.
- The properties of anhydrite for Rock D are taken identical to those obtained for Rock C.
- The properties of quartz are taken from Tazi³⁹: $M = 97.0$ GPa to calculate the homogenized modulus of Rocks E and F.
- The total porosity of Rock F is assumed to be equally distributed between macroporosity (ϕ_{macro}) and microporosity (ϕ_{micro}).

Note that those assumptions on the mineral properties have little impact on the calculated homogenized modulus since the volume fraction of those phases is 3.7% at most (see Table 1). The effect of the last assumption is discussed in the next section.

4.3. Homogenization Results

The homogenized Young's moduli, E_{hom}^{MT} and E_{hom}^{SC} , are calculated by considering Mori-Tanaka (Equations 6 and 7) and self-consistent schemes (Equations 8 and 9), respectively. The ratios of these moduli with respect to the experimental values obtained from macroscopic mechanical tests are presented in Figure 14. These plots show that the global trend of Young's modulus is captured in the sense that the homogenized moduli are roughly proportional to the measured ones. In other words, the homogenization technique, fed with the data obtained from coupling nanoindentation and SEM-EDS analyses, can predict if a rock is stiffer than another one. These results suggest that the rock's mineral composition and properties are key parameters governing the elastic behavior and are responsible for the dispersion of Young's moduli presented in Figure 1. However, we observe that the homogenized moduli predicted with upscaling models overestimate the one measured with macroscopic experiments, using both Mori-Tanaka and self-consistent models. The mean overestimation factor is 1.78 for Mori-Tanaka and 1.72 for self-consistent schemes, and their standard deviations are 0.23 and 0.24, respectively. Despite that this factor is lower in the latter case, various homogenization schemes yield quite similar moduli, suggesting that the phases' spatial organization with respect to each other does not seem to have a significant impact on the homogenized moduli.

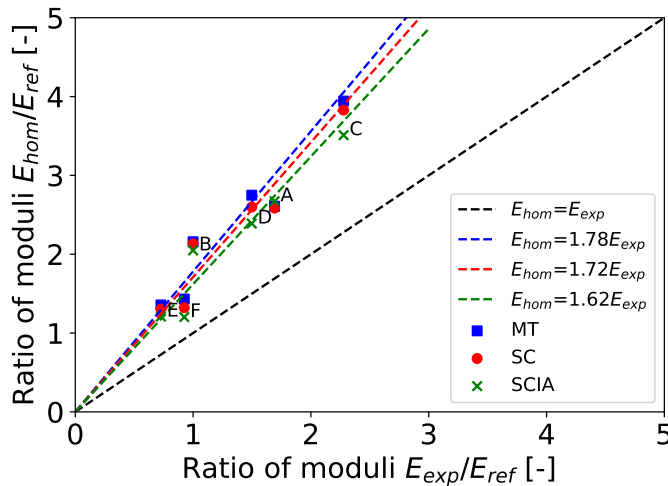


Figure 14: Comparison of the homogenized moduli with the macroscopic experimental ones of the six studied rocks, all normalized with a reference value E_{ref} . Homogenization is performed using Mori-Tanaka (MT) and self-consistent (SC) models, and through the self-consistent indentation approach (SCIA).

To explore the impact on the homogenized moduli of the threshold diameter between microporosity and macroporosity, we vary the threshold over the whole diameter range (Figure 9). In other words, the whole range of porosity distribution between macro and microporosity is explored, leading to the relative errors for each rock given in Figure 15. For the Mori-Tanaka model, the error is lower than 3% for all the rocks. In contrast, these errors are slightly higher using the self-consistent model - as expected - and can reach 6.7% as for Rock F. In conclusion, the impact of the assumption of the diameter threshold on the homogenized moduli is not found to be significant. The sensitivity to Poisson's ratios is studied by varying their value from 0.25 to 0.35 for the three major minerals (calcite, dolomite, anhydrite). For both Mori-Tanaka and self-consistent schemes, the maximum error is about $\pm 3\%$, which is also not significant.

Finally, the homogenization has been performed using the self-consistent indentation approach proposed by Randall et al.⁵⁵. To do so, for every single sample, all the nanoindentation tests were gathered from all the grids. Only those having suitable shapes for their force-penetration curves were retained (i.e., the first stage of test removal presented in Section 2.5). These retained tests are assumed to represent the solid phases of the rock. At the location of each indent, we assume a Poisson's ratio $\nu = 0.3$, which is the Poisson's ratio of all minerals but quartz. The

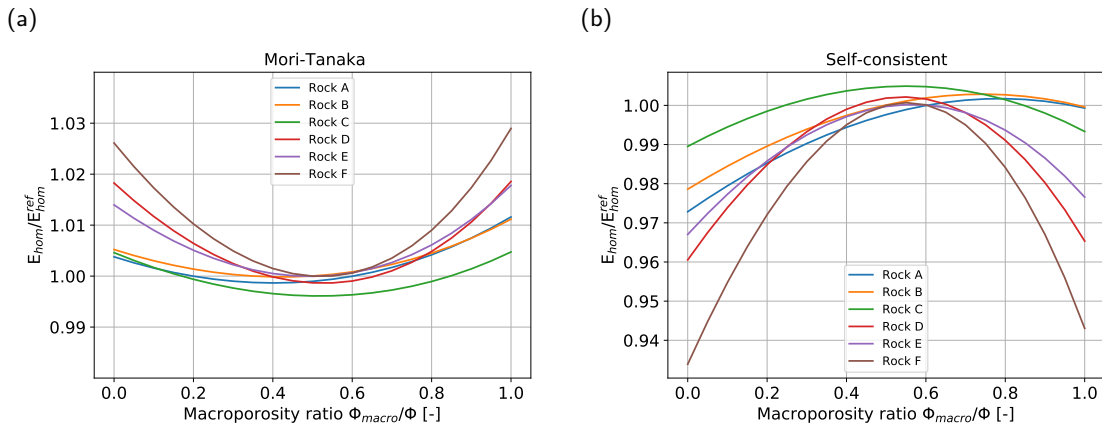


Figure 15: Relative errors linked to the distribution of porosity between macro and microporosity for **(a)** Mori-Tanaka and **(b)** self-consistent schemes. E_{hom}^{ref} stands for the homogenized Young's modulus obtained for the porosity diameter threshold set to 2 μm .

428 Poisson's ratio of quartz is, in fact, equal to 0.08⁵⁶. Still, the volume fraction of quartz is so low in all rocks
 429 considered (see Table 1) that the impact of the Poisson's ratio of quartz on the calculated homogenized modulus
 430 is negligible. To account for porosity, we introduce a phase with vanishing properties and a volume fraction equal
 431 to the global porosity given in Figure 1.

432 The ratios of the corresponding macroscopic homogenized Young's modulus to the experimental one are
 433 presented in Figure 14 for the six rocks. A mean overestimation factor of 1.62 is obtained with this approach,
 434 with a standard deviation of 0.24. The results indicate that the self-consistent indentation approach gives a
 435 very close estimation to that obtained with homogenization schemes applied after proper identification of the
 436 material's various mineralogical phases. Like those latter approaches, the self-consistent indentation approach
 437 can successfully predict if a rock is stiffer than another without requiring any direct characterization of the rock
 438 microstructure (but for the total porosity). This approach is convenient, although it provides less insight into the
 439 physical origin of the dispersion of Young's modulus. Anyhow, we found that the macroscopic elastic properties
 440 of the rocks are overestimated by homogenization, independent of whether homogenization is performed directly
 441 on the indentation grid (i.e., self-consistent indentation approach) or whether homogenization is performed after
 442 proper identification of the various mineralogical phases and their spatial organization.

443 5. Discussion and Exploratory Analyses

444 As seen in the previous section, the homogenized Young's moduli overestimate the measured ones. Many
445 microstructural attributes can explain this result, such as:

- 446 • **The existence of cracks:** the media in the schemes are not considered fractured. However, cracks may exist
447 in the phases, which would reduce the homogenized Young's modulus^{57,58}.
- 448 • **The shape of the pores:** a spherical shape has been assumed for the phases in our homogenization procedure.
449 However, the pore shapes observed in the SEM images are non-regular in most cases (e.g., Figures 6 and
450 7). For example, one can expect that pores' asphericity would reduce the predicted macroscopic Young's
451 modulus⁵⁹.
- 452 • **Interfaces behavior:** Perfect bonding among the phases is assumed in the homogenization models. This
453 assumption is strong and may cause an overestimation of Young's modulus. One can expect that relaxing
454 it (i.e., considering that there can be some discontinuity of displacements or stresses across an interface
455 between phases) would reduce the estimated modulus⁶⁰.

456 Introducing additional complexities translates into introducing additional parameters in the homogenization
457 models. Despite being theoretically developed, the drawback of all these enhancements in homogenization is
458 evaluating the introduced parameters from experimental methods. However, the impact of the first two factors listed
459 above on homogenized Young's modulus is explored in the following subsections. Since the results of section 4
460 showed that the homogenization scheme had little impact on the homogenized results, this exploratory analysis
461 is limited to one homogenization scheme, namely the Mori-Tanaka, which is computationally simpler than the
462 self-consistent scheme.

463 5.1. Cracked Media

Expressions of the homogenized elastic moduli for a medium containing 3-D randomly oriented elliptic cracks
have been developed and given by Pan and Weng⁵⁹. A crack is assumed to have an ellipsoidal shape, with negligible
thickness t and width w in comparison to the length l . Following Budiansky and O'connell⁶¹, a crack density
parameter η is defined in terms of the crack properties as following:

$$\eta = \frac{2N}{\pi} \frac{A^2}{P} \quad (10)$$

where N represents the number of cracks per unit volume, $A = \pi wl$ is the crack area, and $P = 4l$ is its perimeter.
The parameter η is somehow an indicator for the presence of cracks, as it increases when N becomes greater for
uniform crack geometry or when cracks become larger for constant N . The expressions of the homogenized moduli
in the case of a Mori-Tanaka scheme are given in terms of the elastic properties of the matrix and the parameter η
as following:

$$K_{hom}^{\eta} = \frac{K_{mat}}{1 + \frac{16}{9} \frac{1-\nu_{mat}^2}{1-2\nu_{mat}} \eta} \quad (11)$$

$$G_{hom}^{\eta} = \frac{G_{mat}}{1 + \frac{8}{45} (10 - 7\nu_{mat}) \eta} \quad (12)$$

464 As a first qualitative approach, we consider elliptic cracks randomly oriented in the dominant phase of each rock
465 at a lower scale (Scale 0 in Figures 13c and 13d). The ratios of the homogenized modulus to the macroscopic
466 measured one are plotted for each rock in Figure 16. We observe that homogenization estimates the measured
467 values for η ranging between 0.32 and 0.82. The results are consistent with the intensity of overestimation by the
468 initial Mori-Tanaka model, i.e., the higher the overestimation, the greater the density parameter (see Figure 14). It
469 is noticeable that η is the same for Rocks C and D (Facies F2) but exhibits a dispersion for rocks of Facies F1.

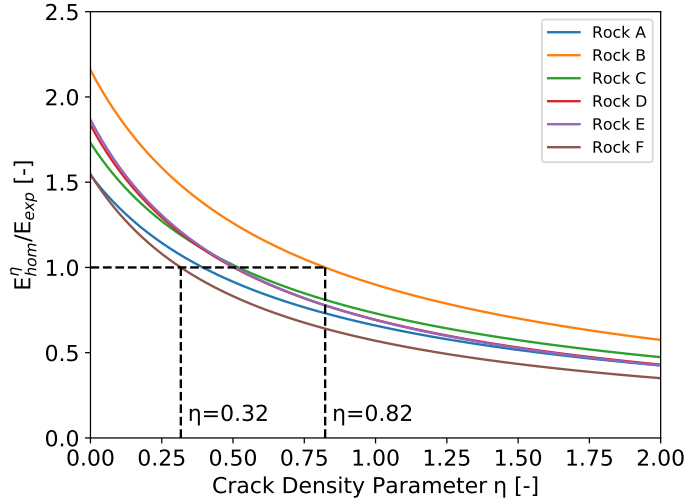


Figure 16: Homogenization results taking into account cracks in the dominant phase of each rock.

470 5.2. Spheroidal Pore Shapes

Pores are now assumed to have spheroidal shapes instead of spherical ones. This shape is illustrated in Figure 17a, where $a_2 = a_3$ and the aspect ratio is defined as:

$$\alpha = \frac{a_1}{a_2} \quad (13)$$

471 Two cases can be distinguished depending on the value of this aspect ratio:

- 472 • The oblate shape for $\alpha < 1$.
- 473 • The prolate shape for $\alpha > 1$.

When the aspect ratio is equal to 1, the shape degenerates to a spherical one. The homogenization solution for a Mori-Tanaka scheme of a matrix containing 3-D randomly oriented spheroidal inclusions has been given by Tandon and Weng⁵⁷ and detailed later with examples in Zhao et al.⁶² for the case of spheroidal pores. The expressions of the homogenized moduli are:

$$K_{hom}^\alpha = \frac{K_{mat}}{1 + \phi.p} \quad (14)$$

$$G_{hom}^\alpha = \frac{G_{mat}}{1 + \phi.q} \quad (15)$$

474 where ϕ is the porosity, p and q are two expressions depending on the Eshelby tensor of a spheroidal inclusion.
475 These expressions can be found in Zhao et al.⁶² and in the shared Python script.

476 For the sake of simplicity, porosity is assumed to be completely present at Scale 1 of the schemes illustrated in
477 Figures 13a and 13b (i.e., $\phi = \phi_{micro}$). It has been shown that the impact of such assumption is not significant on the
478 homogenized moduli in the case of the Mori-Tanaka model (Figure 15). Equations 14 and 15 can thus be used and
479 the ratios of homogenized over measured Young's modulus are plotted in Figure 17b. In agreement with the results
480 published by Zhao et al.⁶², the stiffest medium is obtained in the case of spherical pores, which also corresponds to
481 the upper bound of Hashin and Shtrikman⁵⁷. In the case of oblate pores, the modulus rapidly decreases at a given
482 porosity. However, considering prolate pores instead of spherical ones induces only a slight decrease in the material

483 stiffness. We observe that homogenization estimates Young's modulus's measured values for aspect ratios ranging
 484 from 0.033 to 0.103. As expected, the higher the initial overestimation factor (Figure 14), the lower the pore aspect
 485 ratio. However, the microstructures of the rocks inspected with SEM (Figures 6 to 8) indicate that the aspect ratio
 486 of the pores is much closer to one than those predicted by the inverse analysis performed here. Therefore, it would
 487 be interesting to consider more complex morphologies of pores, which consider an angular character (e.g., see Du
 488 et al.⁶³ for concave pores).

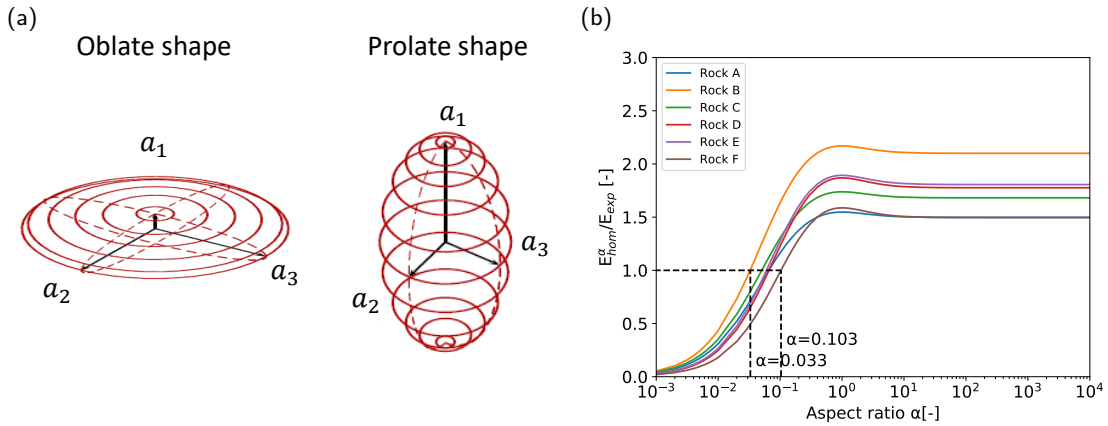


Figure 17: (a) Schematic of the spheroidal shape (from Barthelemy⁶⁴); (b) Homogenization results taking into account randomly oriented spheroidal micropores ($\phi = \phi_{micro}$).

489 5.3. Increasing the Studied Scale - Microindentation Tests

490 The nanoindentation tests of this study have been performed at a shallow penetration depth (200 nm), and the
 491 measured maximum force is around six mN (obtained while indenting the dolomite phase). These tests have been
 492 assumed to probe non-cracked solid subvolumes at a scale of around 2 μm . To account for cracks and porosity, the
 493 probed subvolume must be enlarged by performing microindentation tests at higher levels of penetration depths (or
 494 equivalently force). If this subvolume becomes large enough to be statistically representative of the microstructure,
 495 we would expect to measure the macroscopic elastic properties of the rock directly from the microindentation tests.
 496 The existence of such subvolume is sought for Rocks A, B, and C through microindentation tests performed using
 497 a NHT³ tester in the laboratory of Anton Paar GmbH up to 5 maximum force levels: 0.3 N, 1 N, 3 N, 10 N, and 30
 498 N. For each loading level, ten tests are carried out in different zones chosen randomly on the surface of the polished
 499 samples. Therefore, 50 measurements are obtained for each sample.

500 The results are gathered with those of nanoindentation tests and are presented in Figure 18. Each point on the plots
 501 corresponds to the average value calculated over all the tests performed up to a loading level. The characteristic
 502 size of the probed volume is assumed to be ten times the maximum penetration depth. The results show a high
 503 dispersion, as the coefficient of variation of the microindentation Young's modulus and hardness can reach 20%
 504 and 45%, respectively (Figures 18c and 18d). In addition, these coefficients do not seem to decrease while increasing
 505 the characteristic size, which may be explained by the fact that the scale probed by the deepest microindentations
 506 is not sufficiently large compared to the scale of heterogeneity of microstructures (see Figure 5). Nonetheless,
 507 despite this dispersion, the plots of the mean value of indentation Young's modulus over macroscopic Young's
 508 modulus E_{exp} in Figures 18a and 18b show that while increasing the scale of the study, the indentation modulus
 509 becomes closer to the macroscopic value measured from triaxial experiments E_{exp} . However, the scale reached
 510 by microindentation is not sufficient to predict the macroscopic modulus. The convergence of Young's modulus
 511 of Rock B seems slower than that of Rocks A and C. This observation may be explained by the more pronounced
 512 microstructural heterogeneity of Rock B (see Section 3.1).

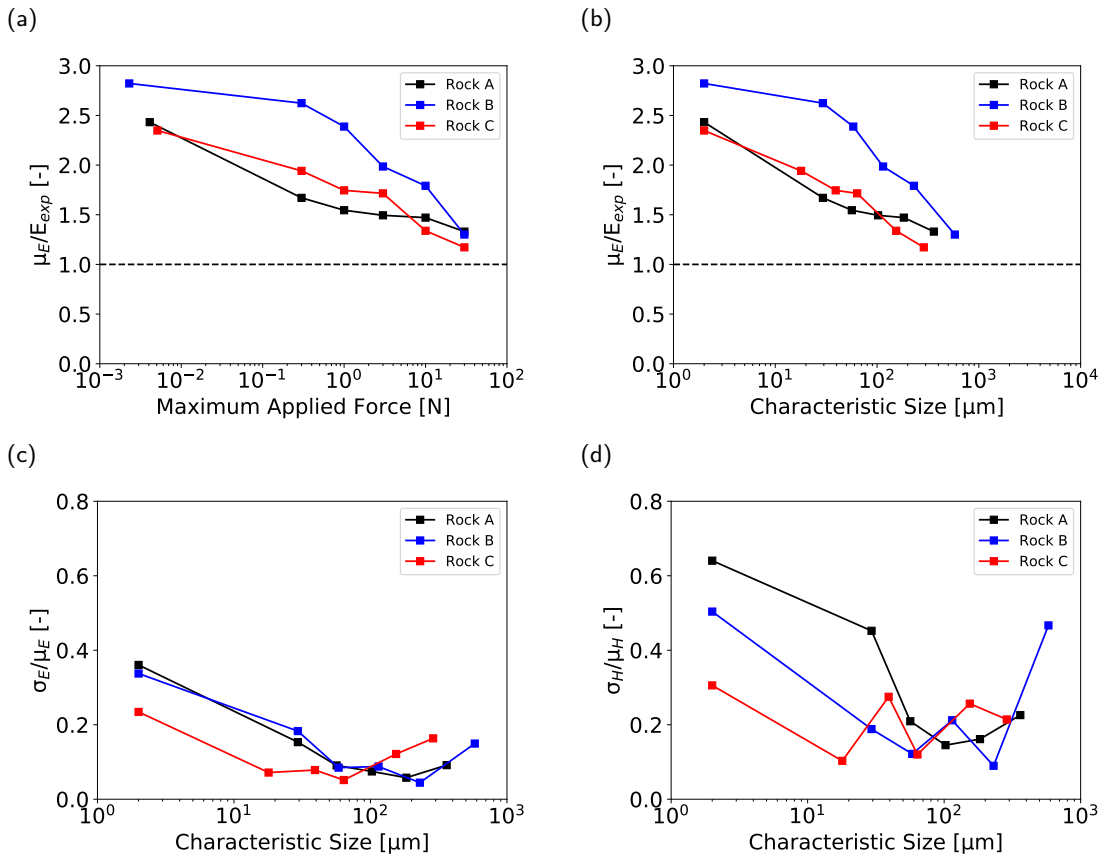


Figure 18: Microindentation and nanoindentation results obtained on Rocks A, B and C: Ratio of the mean indentation Young's modulus μ_E over E_{exp} measured from macroscopic mechanical experiments plotted against (a) the maximum applied force; (b) the characteristic size of the probed volume. Coefficient of variation of the (c) indentation Young's modulus; (d) indentation hardness, with respect to the characteristic size of the probed volume.

6. Conclusions

From a methodological point of view, we have shown that the nanoindentation technique can be applied to carbonate rocks with a wide range of porosities and microstructures. In conjunction with SEM-EDS analyses, we have also shown that nanoindentation could yield valuable information regarding the mechanical properties of the rock's phases. This piece of information made it possible to shed light on the microscopic origin of the dispersion of macroscopic elastic properties. As a perspective, nanoindentation combined with SEM-EDS analysis can be applied, beyond carbonate rocks, to a wide range of heterogeneous materials. Besides, the main conclusions of this study are listed in the following:

1. A full experimental program is developed to couple the indentation measurements and SEM-EDS mapping. The protocol is enriched to solve several issues that the experimenter encounters and provide all the inputs required for homogenization.
2. The mineral composition and mechanical properties of carbonate rocks are main microstructural features controlling the macroscopic elastic properties. Two rocks having the same global porosity can have different proportions of mineral phases and/or different mineral mechanical properties, leading to a significant variation of their macroscopic elastic properties. Dolomite is found to be harder and stiffer than calcite, and a presence of such a phase would reinforce carbonate rocks.
3. The homogenization theory is applied in this study to predict the macroscopic Young's moduli of the rocks. Results show that this technique applied on data obtained at the submicron scale can successfully capture

the macroscopic Young's modulus trend in the sense that it can indicate if a rock is more or less stiff than another one. However, an overestimation of a factor around 1.78 ± 0.23 (in Mori-Tanaka case) and 1.72 ± 0.24 (in self-consistent case) is systematically obtained between the homogenized and measured macroscopic ones.

4. Homogenization through self-consistent indentation approach proposed by Randall et al.⁵⁵ is found to give very close results to those obtained through upscaling schemes fed with the procedure combining nanoindentation and SEM-EDS imaging, and identifying the various mineralogical phases, their volume fractions, mechanical properties, and spatial organization. The former approach is quicker, simpler, and can predict if a rock is stiffer than another. However, the combined nanoindentation and SEM-EDS imaging approach, although more complex, provides greater insight into the physical origin of the dispersion of the macroscopic Young's modulus.
5. Some microstructural features that can explain the macroscopic Young's modulus overestimation are listed, and two of them are investigated: the presence of cracks and the non-spherical shape of pores. Accounting for cracks with a crack density parameter between 0.32 and 0.82 is required to predict a macroscopic Young's modulus of carbonate rocks consistent with the measured ones. However, it is difficult to measure this parameter directly from image analysis. As for the pore geometry feature, spheroidal pores with aspect ratios ranging from 0.033 and 0.104 randomly oriented in the space permit the prediction of the measured macroscopic modulus. However, these aspect ratios do not seem realistic, as the observed pores in the SEM images suggest that the pores are much less aspherical than back-calculated from modeling.
6. The scale of study has been enlarged through microindentation tests. Although the indentation elastic modulus becomes closer to the macroscopic value when the indentation depth increases, microindentation does not seem to reach a scale sufficiently large to make it possible to measure the macroscopic Young's modulus of carbonate rocks directly.

A. Geometric Transformation to Find the Positions of the Indentation Imprints

The indentation grids no longer have a regular square shape in the SEM images. Thus, a geometric transformation of the square to a random quadrangle is proposed based on the corners' positions. A schematic illustration is given in Figure 19.

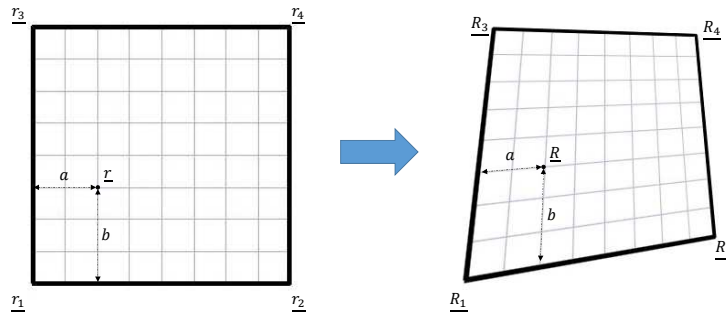


Figure 19: Schematic of the considered geometric transformation to calculate the positions of all the imprints of a grid.

Let $(\underline{r}_i)_{i=1,2,3,4}$ and $(\underline{R}_i)_{i=1,2,3,4}$ denote the position vectors of the four corners before and after the transformation, respectively. Let \underline{r} and \underline{R} denote the position vectors of an intermediate point (or an imprint in our case) before and after the transformation, respectively. In the initial configuration, \underline{r} can be expressed in terms of the coordinates of the four corners as:

$$\begin{aligned} \underline{r} = & \underline{r}_1 + a \left[(1 - b)(\underline{r}_2 - \underline{r}_1) + \frac{b}{2}(\underline{r}_4 - \underline{r}_1) \right] \\ & + b \left[(1 - a)(\underline{r}_3 - \underline{r}_1) + \frac{a}{2}(\underline{r}_4 - \underline{r}_1) \right] \end{aligned} \quad (16)$$

where the parameters a and b vary between 0 and 1. When these parameters take simultaneously the values of 0 and/or 1, the position vector is nothing else than that of one of the corners. Likewise, the coordinates of the same

point in the deformed configuration can be expressed using the same values for a and b , such as:

$$\underline{R} = \underline{R}_1 + a \left[(1-b)(\underline{R}_2 - \underline{R}_1) + \frac{b}{2}(\underline{R}_4 - \underline{R}_1) \right] + b \left[(1-a)(\underline{R}_3 - \underline{R}_1) + \frac{a}{2}(\underline{R}_4 - \underline{R}_1) \right] \quad (17)$$

Since the position vectors of the 4 corners are known in both configurations, the evaluation of a and b can be done using Equation 16 and the identification of the vector position \underline{R} is straightforward using Equation 17.

Acknowledgment

This work was carried out with funding from Total (now TotalEnergies SE). We thank Pierre Barlet from TotalEnergies SE for the triaxial tests.

Conflict of Interest

The authors declare that there are no known conflicts of interest associated with this publication.

Code Availability

Python scripts relative to the current article are available for interested readers at the following link: <https://doi.org/10.5281/zenodo.4452014>.

References

1. Wilkinson BH, McElroy BJ, Kesler SE, Peters SE, Rothman ED. Global geologic maps are tectonic speedometers - Rates of rock cycling from area-age frequencies. *Geological Society of America Bulletin* 2009;121(5-6):760–779. doi:10.1130/B26457.1.
2. Tester JW, Anderson BJ, Batchelor A, Blackwell D, DiPippo R, Drake E, Garnish J, Livesay B, Moore M, Nichols K, et al. The future of geothermal energy. *Massachusetts Institute of Technology* 2006;358.
3. Rutqvist J. The geomechanics of CO2 storage in deep sedimentary formations. *Geotechnical and Geological Engineering* 2012;30(3):525–551. doi:10.1007/s10706-011-9491-0.
4. Choquette PW, Pray LC. Geologic nomenclature and classification of porosity in sedimentary carbonates. *AAPG bulletin* 1970;54(2):207–250. doi:10.1306/5D25C98B-16C1-11D7-8645000102C1865D.
5. Eberli GP, Baechle GT, Anselmetti FS, Incze ML. Factors controlling elastic properties in carbonate sediments and rocks. *The Leading Edge* 2003;22(7):654–660. doi:10.1190/1.1599691.
6. Flügel E. *Microfacies of carbonate rocks: analysis, interpretation and application*. Berlin: Springer Science & Business Media; 2004.
7. Weger RJ, Eberli GP, Baechle GT, Massaferro JL, Sun YF. Quantification of pore structure and its effect on sonic velocity and permeability in carbonates. *AAPG bulletin* 2009;93(10):1297–1317. doi:10.1306/05270909001.
8. Fournier F, Leonide P, Biscarrat K, Gallois A, Borgomano J, Foubert A. Elastic properties of microporous cemented grainstones. *Geophysics* 2011;76(6):E211–E226. doi:10.1190/geo2011-0047.1.
9. Kalo K, Grgic D, Auvray C, Giraud A, Drach B, Sevostianov I. Effective elastic moduli of a heterogeneous oolitic rock containing 3-D irregularly shaped pores. *International Journal of Rock Mechanics and Mining Sciences* 2017;98:20–32. doi:10.1016/j.ijrmmms.2017.07.009.
10. Ulm FJ, Vandamme M, Bobko C, Alberto Ortega J, Tai K, Ortiz C. Statistical indentation techniques for hydrated nanocomposites: concrete, bone, and shale. *Journal of the American Ceramic Society* 2007;90(9):2677–2692. doi:10.1111/j.1551-2916.2007.02012.x.
11. Ma Z, Gamage RP, Zhang C. Application of nanoindentation technology in rocks: a review. *Geomechanics and Geophysics for Geo-Energy and Geo-Resources* 2020;6(4):1–27. doi:10.1007/s40948-020-00178-6.
12. Vialle S, Lebedev M. Heterogeneities in the elastic properties of microporous carbonate rocks at the microscale from nanoindentation tests. In: *SEG Technical Program Expanded Abstracts 2015*. Society of Exploration Geophysicists; 2015:3279–3284.
13. Zhang Y, Lebedev M, Al-Yaseri A, Yu H, Nwideo LN, Sarmadivaleh M, Barifcani A, Iglauer S. Morphological evaluation of heterogeneous oolitic limestone under pressure and fluid flow using X-ray microtomography. *Journal of Applied Geophysics* 2018;150:172–181. doi:10.1016/j.jappgeo.2018.01.026.
14. Lebedev M, Wilson ME, Mikhaltsevitch V. An experimental study of solid matrix weakening in water-saturated Savonnières limestone: Solid matrix weakening in water-saturated limestone. *Geophysical Prospecting* 2014;62(6):1253–1265. doi:10.1111/1365-2478.12168.
15. Lebedev M, Zhang Y, Sarmadivaleh M, Barifcani A, Al-Khdheawi E, Iglauer S. Carbon geosequestration in limestone: Pore-scale dissolution and geomechanical weakening. *International Journal of Greenhouse Gas Control* 2017;66:106–119. doi:10.1016/j.ijggc.2017.09.016.

- 603 16. Zhang Y, Lebedev M, Sarmadivaleh M, Barifcani A, Iglauer S. Change in geomechanical properties of limestone due to supercritical
604 CO₂ injection. In: *SPE Asia Pacific Oil & Gas Conference and Exhibition*. OnePetro; 2016:.
- 605 17. Vialle S, Pazdniakou A, Adler P, et al. Prediction of the macroscopic mechanical properties of carbonate from nano-indentation tests. In:
606 *52nd US Rock Mechanics/Geomechanics Symposium*. American Rock Mechanics Association; 2018:.
- 607 18. Doube M, Firth EC, Boyde A, Bushby AJ. Combined nanoindentation testing and scanning electron microscopy of bone and articular
608 calcified cartilage in an equine fracture predilection site. *European cells materials* 2010;19:242–51. doi:10.22203/ecm.v019a23.
- 609 19. Yang C, Xiong Y, Wang J, Li Y, Jiang W. Mechanical characterization of shale matrix minerals using phase-positioned nanoindentation
610 and nano-dynamic mechanical analysis. *International Journal of Coal Geology* 2020;229:103571. doi:10.1016/j.coal.2020.
611 103571.
- 612 20. Liu Y, Liu A, Liu S, Kang Y. Nano-scale mechanical properties of constituent minerals in shales investigated by combined nanoindentation
613 statistical analyses and sem-edx-rxd techniques. *International Journal of Rock Mechanics and Mining Sciences* 2022;159:105187.
614 doi:10.1016/j.ijrmmms.2022.105187.
- 615 21. Abedi S, Slim M, Hofmann R, Bryndzia T, Ulm FJ. Nanochemo-mechanical signature of organic-rich shales: a coupled indentation–edx
616 analysis. *Acta Geotechnica* 2016;11(3):559–572. doi:10.1007/s11440-015-0426-4.
- 617 22. Mashhadani M, Verde A, Sharma P, Abedi S. Assessing mechanical properties of organic matter in shales: Results from coupled
618 nanoindentation/sem-edx and micromechanical modeling. *Journal of Petroleum Science and Engineering* 2018;165:313–324. doi:10.
619 1016/j.petro.2018.02.039.
- 620 23. Veytskin YB, Tammina VK, Bobko CP, Hartley PG, Clennell MB, Dewhurst DN, Dagastine RR. Micromechanical characterization of
621 shales through nanoindentation and energy dispersive x-ray spectrometry. *Geomechanics for Energy and the Environment* 2017;9:21–35.
622 doi:https://doi.org/10.1016/j.gete.2016.10.004.
- 623 24. Kumar V, Sondergeld CH, Rai CS. Nano to Macro Mechanical Characterization of Shale. SPE Annual Technical Conference and
624 Exhibition; 2012:doi:10.2118/159804-MS.
- 625 25. Mason J, Carloni J, Zehnder A, Baker SP, Jordan T. Dependence of Micro-Mechanical Properties on Lithofacies: Indentation Experiments
626 on Marcellus Shale. SPE/AAPG/SEG Unconventional Resources Technology Conference; 2014:doi:10.15530/URTEC-2014-1922919;
627 uRTEC-1922919-MS.
- 628 26. Chen JJ, Sorelli L, Vandamme M, Ulm FJ, Chanvillard G. A coupled nanoindentation/sem-edx study on low water/cement ratio
629 portland cement paste: evidence for c–s–h/ca (oh) 2 nanocomposites. *Journal of the American Ceramic Society* 2010;93(5):1484–1493.
630 doi:10.1111/j.1551-2916.2009.03599.x.
- 631 27. Wilson W, Rivera-Torres J, Sorelli L, Durán-Herrera A, Tagnit-Hamou A. The micromechanical signature of high-volume natural
632 pozzolan concrete by combined statistical nanoindentation and sem-edx analyses. *Cement and Concrete Research* 2017;91:1–12.
633 doi:https://doi.org/10.1016/j.cemconres.2016.10.004.
- 634 28. Moser RD, Allison PG, Chandler MQ. Characterization of impact damage in ultra-high performance concrete using spatially
635 correlated nanoindentation/sem/edx. *Journal of Materials Engineering and Performance* 2013;22(12):3902–3908. doi:10.1007/
636 s11665-013-0668-y.
- 637 29. Zhang Y, Liang M, Gan Y, Çopuroğlu O. Micro-mechanical properties of slag rim formed in cement-slag system evaluated by
638 nanoindentation combined with sem. *Materials* 2022;15(18). doi:10.3390/ma15186347.
- 639 30. Sorelli L, Pham DT, Vallée D, Chen J, Fafard M. Finite Element Based Characterization of the Creep Properties of the Cement Paste
640 Phases by Coupling Nanoindentation Technique and SEM-EDS. 2013:182–189. doi:10.1061/9780784413111.021.
- 641 31. Bu Y, Saldana C, Handwerker C, Weiss J. The Role of Calcium Hydroxide in the Elastic and Viscoelastic Response of Cementitious
642 Materials: A Nanoindentation and SEM-EDS Study. In: Sobolev K, Shah SP, eds. *Nanotechnology in Construction*. Cham: Springer
643 International Publishing. ISBN 978-3-319-17088-6; 2015:25–34.
- 644 32. Deirieh A, Ortega JA, Ulm FJ, Abousleiman Y. Nanochemomechanical assessment of shale: a coupled WDS-indentation analysis. *Acta*
645 *Geotechnica* 2012;7(4):271–295. doi:10.1007/s11440-012-0185-4.
- 646 33. Krakowiak KJ, Wilson W, James S, Musso S, Ulm FJ. Inference of the phase-to-mechanical property link via coupled X-ray
647 spectrometry and indentation analysis: Application to cement-based materials. *Cement and Concrete Research* 2015;67:271–285.
648 doi:10.1016/j.cemconres.2014.09.001.
- 649 34. Cała M, Cyran K, Kawa M, Kolano M, Łydzba D, Pachnicz M, Rajczakowska M, Rózański A, Sobótka M, Stefaniuk D, et al. Identification
650 of microstructural properties of shale by combined use of X-ray micro-CT and nanoindentation tests. *Procedia engineering* 2017;191:735–
651 743. doi:10.1016/j.proeng.2017.05.239.
- 652 35. Ahmadov R, Vanorio T, Mavko G. Confocal laser scanning and atomic-force microscopy in estimation of elastic properties of the
653 organic-rich bazhenov formation. *The Leading Edge* 2009;28(1):18–23. doi:10.1190/1.3064141.
- 654 36. Shukla P, Kumar V, Curtis M, Sondergeld CH, Rai CS, et al. Nanoindentation studies on shales. In: *47th US Rock Mechan-*
655 *ics/Geomechanics Symposium*. American Rock Mechanics Association; 2013:.
- 656 37. Constantinides G, Chandran KR, Ulm FJ, Van Vliet K. Grid indentation analysis of composite microstructure and mechanics: Principles
657 and validation. *Materials Science and Engineering: A* 2006;430(1-2):189–202. doi:10.1016/j.msea.2006.05.125.
- 658 38. Lura P, Trtik P, Münch B. Validity of recent approaches for statistical nanoindentation of cement pastes. *Cement and Concrete Composites*
659 2011;33(4):457–465. doi:10.1016/j.cemconcomp.2011.01.006.
- 660 39. Tazi H. Propriétés élastiques et anisotropie des roches mères : approche expérimentale multi-échelle et modélisation par milieu effectif.
661 PhD dissertation; Université Paris-Est; 2019. URL: <https://pastel.archives-ouvertes.fr/tel-02878713>.
- 662 40. Rugar D, Hansma P. Atomic force microscopy. *Physics today* 1990;43(10):23–30.
- 663 41. Nguyen DL. Nouvelle méthodologie d'identification des propriétés mécaniques locales d'un matériau hétérogène par nanoindentation -
664 application aux matériaux du génie civil. PhD dissertation; Université Paris-Est; 2017. URL: <https://pastel.archives-ouvertes.fr/tel-01730567>.

- 666 42. Miller M, Bobko C, Vandamme M, Ulm FJ. Surface roughness criteria for cement paste nanoindentation. *Cement and Concrete Research* 2008;38(4):467–476. doi:10.1016/j.cemconres.2007.11.014.
- 667 43. Donnelly E, Baker SP, Boskey AL, van der Meulen MC. Effects of surface roughness and maximum load on the mechanical properties of
- 668 cancellous bone measured by nanoindentation. *Journal of Biomedical Materials Research Part A: An Official Journal of The Society for*
- 669 *Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials*
- 670 *2006;77(2):426–435. doi:10.1002/jbm.a.30633.*
- 671 44. VanLandingham MR. Review of instrumented indentation. *Journal of Research of the National Institute of Standards and Technology*
- 672 *2003;108(4):249. doi:10.6028/jres.108.024.*
- 673 45. Larson P, Giannakopoulos A, Söderlund E, Rowcliffe D, Vestergaard R. Analysis of berkovich indentations. *Int J Solids Struct*
- 674 *1996;33:221–248. doi:10.1016/0020-7683(95)00033-7.*
- 675 46. Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing
- 676 indentation experiments. *Journal of materials research* 1992;7(6):1564–1583. doi:10.1557/JMR.1992.1564.
- 677 47. Tabor D. The hardness of metals. Oxford university press; 2000.
- 678 48. Ganneau F, Constantinides G, Ulm FJ. Dual-indentation technique for the assessment of strength properties of cohesive-frictional
- 679 materials. *International journal of solids and structures* 2006;43(6):1727–1745. doi:10.1016/j.ijsolstr.2005.03.035.
- 680 49. Fialips CI, Labeyrie B, Burg V, Mazière V, Munerel Y, Haurie H, Jolivet I, Lasnel R, Laurent JP, Lambert L, Jacquelin-Vallée L.
- 681 Quantitative Mineralogy of Vaca Muerta and Alum Shales From Core Chips and Drill Cuttings by Calibrated SEM-EDS Mineralogical
- 682 Mapping. In: *Proceedings of the 6th Unconventional Resources Technology Conference*. Houston, Texas, USA: American Association
- 683 of Petroleum Geologists. ISBN 978-0-9912144-5-7; 2018;doi:10.15530/urtec-2018-2902304.
- 684 50. Delesse M. Procédé mécanique pour déterminer la composition des roches. *CR Acad Sci Paris* 1847;25:544–545.
- 685 51. Zaoui A. Matériaux hétérogènes et composites: majeure de mécanique, option matériaux et structures: promotion 1998, majeure 1, 2e
- 686 année. École polytechnique; 2000.
- 687 52. Eshelby JD. The determination of the elastic field of an ellipsoidal inclusion, and related problems. *Proceedings of the royal society of*
- 688 *London Series A Mathematical and physical sciences* 1957;241(1226):376–396.
- 689 53. Mori T, Tanaka K. Average stress in matrix and average elastic energy of materials with misfitting inclusions. *Acta metallurgica*
- 690 *1973;21(5):571–574. doi:10.1016/0001-6160(73)90064-3.*
- 691 54. Hershey A. The elasticity of an isotropic aggregate of anisotropic cubic crystals. *Journal of Applied mechanics-transactions of the ASME*
- 692 *1954;21(3):236–240.*
- 693 55. Randall NX, Vandamme M, Ulm FJ. Nanoindentation analysis as a two-dimensional tool for mapping the mechanical properties of
- 694 complex surfaces. *Journal of materials research* 2009;24(3):679–690. doi:10.1557/jmr.2009.0149.
- 695 56. Gercek H. Poisson's ratio values for rocks. *International Journal of Rock Mechanics and Mining Sciences* 2007;44(1):1–13.
- 696 doi:10.1016/j.ijrmmms.2006.04.011.
- 697 57. Tandon G, Weng G. Average stress in the matrix and effective moduli of randomly oriented composites. *Composites science and*
- 698 *technology* 1986;27(2):111–132. doi:10.1016/0266-3538(86)90067-9.
- 699 58. Dormieux L, Kondo D, Ulm FJ. Microporomechanics. John Wiley & Sons; 2006.
- 700 59. Pan H, Weng G. Elastic moduli of heterogeneous solids with ellipsoidal inclusions and elliptic cracks. *Acta mechanica* 1995;110(1-
- 701 4):73–94. doi:10.1007/BF01215417.
- 702 60. Ghabezloo S. A micromechanical model for the effective compressibility of sandstones. *European Journal of Mechanics-A/Solids*
- 703 *2015;51:140–153. doi:10.1016/j.euromechsol.2014.12.007.*
- 704 61. Budiansky B, O'connell RJ. Elastic moduli of a cracked solid. *International journal of Solids and structures* 1976;12(2):81–97.
- 705 doi:10.1016/0020-7683(76)90044-5.
- 706 62. Zhao Y, Tandon G, Weng G. Elastic moduli for a class of porous materials. *Acta Mechanica* 1989;76(1-2):105–131. doi:10.1007/
- 707 BF01175799.
- 708 63. Du K, Cheng L, Barthélémy JF, Sevostianov I, Giraud A, Adessina A. Effective elastic properties of transversely isotropic materials with
- 709 concave pores. *Mechanics of Materials* 2021;153:103665. doi:10.1016/j.mechmat.2020.103665.
- 710 64. Barthelemy JF. Approche micromécanique de la rupture et de la fissuration dans les géomatériaux. Ph.D. thesis; Ecole des Ponts
- 711 ParisTech; 2005.
- 712