An experimental study of solid matrix weakening in water-saturated Savonnières limestone

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ABSTRACT

Petrophysical properties of carbonate reservoirs are less predictable than that of siliciclastic reservoirs. One of the main reasons for this is the physical and chemical interactions of carbonate rocks with pore fluids. Such interactions can significantly change the elastic properties of the rock matrix and grains, making the applicability of Gassmann’s fluid substitution procedure debatable. This study is an attempt to understand the mechanisms of fluid-rock interactions and the influence of these interactions on elastic parameters of carbonates. We performed precise indentation tests on Savonnières limestone at a microscale level under dry, distilled water, and n-Decane saturated conditions. Our experiments display softening of the rock matrix after water saturation. We have found that mainly the ooid cortices, peloid nuclei and prismatic intergranular cement are affected by water flooding. We also observed a shear modulus reduction in Savonnières limestone in an experiment performed at ultrasonic frequencies. One of the most important results obtained in our experimental study is that the Gassmann fluid substitution theory might not always be applicable to predict the elastic moduli of fluid-saturated limestones.

Key words: Rock physics, Elastics, Petrophysics, Nanoindentation.

INTRODUCTION

It is well known that over geological time reservoir rocks and fluids inside rocks come to physical and chemical equilibrium with each other. Changing thermodynamic conditions such as pressure, temperature, salinity, alkalinity, or fluid replacement in the pore space of rocks will facilitate chemical reactions between fluid and rock material resulting in partial dissolution of rock and/or precipitation of minerals. Mineral composition and microstructure of carbonate rocks are the key factors that determine rock mechanical properties (Rhett and Lord 2001; Vanorio and Mavko 2011). In laboratory studies of the elastic properties of fluid-saturated carbonates conducted at ultrasonic frequencies, the applicability of Gassmann’s relations to carbonate sedimentary rocks was questioned (Wang 1997; Baechle et al. 2005; Adam et al. 2006; Sharma et al. 2006; Vanorio, Scotallero and Mavko 2008; Misaghi et al. 2010; Vialle and Vanorio 2011). Adam et al. 2006 show that viscoelastic properties of fluid-saturated rocks measured at ultrasonic frequencies might differ significantly from the dynamic moduli at seismic frequencies for a small set of carbonate samples. Several laboratory studies have also reported that the shear modulus can be reduced when the rock changes from dry to saturated conditions (Assefa et al. 2003; Røgen et al. 2005; Sharma et al. 2006). The main factors inferred to be responsible for that reduction are carbonate pore types (Wang 1997; Baechle et al. 2005), pore connectivity (Rossebø et al. 2005; Misaghi et al. 2010) and clay content (Jaspen et al. 2002).

The reduction of the shear modulus due to distilled water saturation on a Savonnières limestone was observed in laboratory measurements conducted at seismic frequencies (1 Hz-100 Hz) at a confining pressure of 17 MPa
(Mikhailsevich et al., 2013). Weakening of Savonnières limestone rock matrix due to water vapour was recently reported by Lopes et al. (2014). All of these results violate the main assumption of the Gassmann theory of fluid substitution that the solid matrix should remain the same in dry and fluid-saturated conditions. Research to date, therefore, renders the implementation of water substitution, and applicability of the Gassmann theory in carbonates, problematic. The underlying reasons for the inapplicability of the Gassmann fluid substitution theory for carbonate rocks, however, are not fully clarified. To understand that, it is necessary to find out how fluids affect the elastic moduli of carbonate rocks.

The indentation technique has been widely used over the centuries to estimate the mechanical properties of small areas on the surface of materials (Fischer-Cripps 2004). This technique is based on “contacting” the material (sample) with another material (indenter), where the material properties of the latter are well defined. During mechanical interaction of the indenter with the sample, both elastic and plastic deformation may occur. The geometry and size of the permanent mark remaining on the sample together with the relationship between the applied force and penetration of the indenter into the sample provides information about hardness and indentation modulus. A historical overview and further details of the indentation technique can be found elsewhere (Fischer-Cripps 2004). This technique has been successfully applied to rock sample materials such as shales (Ortega et al. 2007; Akrad et al. 2011; Zargari et al. 2013) and carbonates (Pérez-Huerta et al. 2007; De Paula et al. 2010). In the majority of such experiments the so-called grid-indentation technique is applied (Ortega et al. 2007), in which a statistically significant number of indentation measurements are obtained from a big area of the sample. The elastic moduli of different materials as well as composition of the rock samples are estimated by statistical analysis of data (Durst et al. 2004; Constantinides et al. 2006).

Using the indentation technique, it is possible to measure the mechanical properties of individual elements of the rock due to fluid-rock interaction. Such experiments require in situ monitoring on exact parts of the sample both pre- and post-fluid saturation of the sample since indentation measurements must be undertaken both before and after any potential reactions with fluids. To fill this deficit in experimental data, in this paper, we are reporting the results of our measurements of elastic moduli of dry and water-saturated Savonnières limestone using the indentation method.

**EXPERIMENT**

**Description of Savonnières limestone**

The Savonnières Oolitic Limestone from eastern France is of Jurassic age, deposited around 100 million years ago (Fronteau et al., 2010). On the basis of thin section petrography and scanning electron microscopy, the sample is a partially calcite-cemented oolitic grainstone dominated by near spherical to elliptical ooids up to 6 mm in diameter (Figure 1). These ooids formed through precipitation of concentric layers and/or radial crystal growth of calcium carbonate cement around a pre-existing grain (nuclei; Flügel, 2004 and references therein). There is some alteration of the ooid cortices, preserving ‘ghost fabrics’ of original precipitated ooid layers. Because of this, and since all the aragonitic bioclasts are dissolved, the original ooid precipitate is inferred to have been metastable Mg-calcite now altered to low Mg-calcite. In this sample, ooid shape and size is dependent on: (1) the original shape and size of the nucleus, (2) the degree of oolitic precipitation formation and abrasion, and (3) whether individual ooids have been collectively further overgrown by additional oolitic cortices to form compound ooids. Original nuclei to ooids include peloids (carbonate pellets composed of clay-sized particles) and/or loosely lithified carbonate sediment. Many ooid nuclei have been leached out, some likely after mollusc fragments on the basis of their curved elongate shape. Secondary porosity, due to dissolution, therefore comprises much of the original area of the leached nucleus. Some intra-oolid pores are, however, partially to near-completely filled with micritic (carbonate mud) or fine peloidal sediment. Both superficial (having ooid cortex width distinctly less than half the ooid diameter, often having one or two laminae) and compound ooids are present in the sample. Larger whole articulated and disarticulated bivalves over 1 cm across were also present in the original sediment that were little affected by oolitic precipitation, but were affected by micritisation, prior to dissolution, hence their original shape is preserved by micrite envelopes (Figure 1). After deposition, but prior to dissolution, all sediment grains were cemented via a clear, palisadic calcite cement with the long axis of crystal palisades ~200–300 μm in length that partially occludes primary intergranular porosity (Figure 1). Other authors have noted comparable features in other samples of the Savonnières Limestone: notably the oolitic character, their radial and concentric development, common dissolution of ooid nuclei and pervasive palisadic calcite cements (Roels et al., 2001; Fronteau et al., 2010).
Figure 1 Thin section photomicrograph and scanning electron microscope image (analysis conditions: backscattered electrons, 15kV accelerating voltage, 6.4 mm working distance on SEM Hitachi TM3030 Tabletop SEM) of the Savonnières Oolite showing: (1) Pore space, including palisadic cement lined interparticle pores (ip), combined original shelter porosity from under a shell and leached out biomoldic porosity after dissolution of shell (bp), and intra ooid pores (iop); (2) Concentric layered oolitic cortices (O), ooids include superficial ooids (S) and composite ooid (C); (3) Peloid nucleus to ooid (P); (4) Palisadic fringing cement (F); (5) Partial micrite fill to leaching ooid nuclei and/or micritic envelope to dissolved bivalve (M); (6) Fine peloidal sediment infill of leaching ooid nuclei and/or partially lithified sediment nuclei to ooid (E).
On the basis of the petrological and scanning electron microscopy studies, we identify the following areas with possible different mechanical properties (Figure 1):

1. Pore space, including palisadic cement lined interparticle pores, intra ooid pores and pores that results from a combination of original shelter porosity under shells and biomoldic porosity after leaching of bivalve shells.
2. Concentric layered, or to a lesser extent radially developed, oolitic cortices
3. Peloid nucleus to ooid
4. Palisadic fringing cement
5. Partial micrite fill to leaching ooid nuclei and/or micritic envelope to dissolved bivalve
6. Fine peloidal sediment infill of leached ooid nuclei and/or partially lithified sediment nuclei to ooid.

Ooid precipitation occurs in warm shallow waters, in regions of arid to semi-arid climates where waters become supersaturated with respect to calcium carbonate. Some ooid precipitation may be partially biologically mediated (Flügel, 2004 and references therein). Agitation by currents or waves is inferred due to rounding of the ooids. The presence of peloids as nuclei indicates some derivation of material from low energy settings (Jones and Goodbody, 1984; Steinhoff and Strohmenger, 1996). Superficial ooids tend to form around larger grains, since the latter are seldom moved, and this may be the reason for the paucity of ooid cortex development around many shell fragments or larger peloids (Harris, 1979). Formation of these ooids perhaps occurred under moderate rather than high energy conditions due to the presence of: (a) peloid nuclei, (b) superficial ooids, and (c) evidence for some radial cortex crystal precipitation (Steinhoff and Strohmenger, 1996). Radial ooid cortex development is however also linked to original high Mg-calcite precipitation or variation in the transport mechanism of ooids of different size (Davies et al., 1978; Heller et al., 1980). Diagenesis (sediment alteration), in order of occurrence, is the following: (i) precipitation of ooid cortices; (ii) micritisation (partially contemporaneous with ooid cortex formation); (iii) local compaction of ooid; (iv) palisadic cement formation; (v) dissolution of aragonite.

According to Roels et al. (2003) the Savonnières limestone shows a wide range of pore size distribution: intragranular micropores (typical radius 10^{-7} - 10^{-6} m), intergranular mesopores (10^{-5} m), intergranular macropores (10^{-4} m), and molic macropores (10^{-4} m). Using these same definitions of porosity and on the basis of point counting of thin sections, the studied sample includes \sim 14–21% porosity (intragranular meso/macropores: 5.2–7.4%, combined biomoldic/shelter macropores: 4.0–8.0%). Intergranular microporosity is also present but difficult to quantify from the thin sections, and will additionally contribute to the porosity of the sample. The total porosity in our sample is comparable with that of \sim 18% for a Savonnières Oolite sample studied by Virgin et al. (1996). In contrast, Fronteau et al. (2010) described the Savonnières limestone as being predominantly macroporous with 30–40% porosity.

**Nanoindentation method**

In this experiment we used an IBIS nanoindentation system (Model B, Fisher-Cripps Laboratories Pty.Ltd.) with a Berkovich-type diamond indenter. The Berkovich nanoindentor is a three-sided pyramid with a face angle of 65.27 degrees, measured from the axis to one of the pyramidal faces. Figure 2(a) shows a schematic of the indenter experiment. Typical records acquired during nanoindentation measurements are shown in Figure 2(b-c). By gradually increasing the load (P), the indenter penetrates into the sample, whereby the sample undergoes plastic and elastic deformation during loading (shown as a “loading” curve on Figure 2(c)). A gradual decrease of the applied load leads to stress unloading on the sample.

The so-called indentation modulus (M) can be obtained from the slope (shown as \frac{dP}{db} in Figure 2(b) of the unloading curve at maximum load. Equation (1) shows the indentation modulus as function of the slope and area of contact (A) (Fischer-Cripps, 2004):

\[
M = \frac{1}{2} \pi \frac{dP}{dh}.
\]  

The area of contact at any penetration depth \(h\) of the indenter inside the sample can be calculated from the geometry of the indenter and for Berkovich-type indenters is

\[
A \approx 24.5b^2.
\]

For isotropic media, the indentation modulus (M) can be defined by the following equation (Timoshenko and Goodier, 1951):

\[
\frac{1}{M} = \frac{1}{E_s} + \frac{1}{E_{ind}} - \frac{v_s}{v_{ind}},
\]

where \(E_s\) and \(v_s\), \(E_{ind}\) and \(v_{ind}\) are the Young’s modulus and Poisson’s ratio of the rock and indenter, respectively.

The Young’s modulus of the sample can only be estimated from equation (2) as the Poisson’s ratio of the sample is unknown. When we take into account that Poisson’s ratio
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Figure 2 Indentation technique: (a) Penetration of indenter into the sample during loading. Typical load-unloading curves for two samples: (b) fused silica (Young’s modulus 72.5 GPa, Poisson’s ratio 0.17, measured indentation modulus 74.6 GPa); and (c) Savonnières limestone sample in this study (indentation modulus at this point is 65.4 GPa).

of solids may vary from 0 to 0.5 the maximum and minimum values of Young’s modulus $E_s$ are:

$$0.75M \leq E_s \leq M.$$  

In practice, for most types of rocks the Poisson’s ratio of materials varies from 0.1 to 0.4 leading to a less than 16% difference between the Young’s modulus and the indentation modulus. Sometimes in the literature an indentation modulus is called “reduced modulus”. Such naming, however, may cause confusion as the value of the indentation modulus according to equation (3) is always higher than the Young’s modulus. Finally, our nanoindentation apparatus was calibrated on various homogenous materials with known mechanical properties such as fused silica, individual calcite crystals, copper, aluminium and under a wide range of applied maximum loads from 0.1 mN to 300 mN.

Sample preparation and experimental procedure

A small piece of Savonnières limestone (5 mm x 4 mm x 2 mm) is cut from the big block and hand polished using diamond abrasives paste (3 μm) and aluminium oxide (0.3 μm). The achieved surface roughness of the samples is less than $R_a = 0.15 \mu m$. The optical image of the samples’ surface from binocular microscopy is shown in Figure 3(a). A micro computerized tomographic (micro CT) image of the sample obtained using X-Ray tomograph Versa500XRM (Zeiss – XRadia, Ltd) is presented in Figure 3(b). The micro CT image shows the slice parallel to the surface of the sample but located 0.1 mm under the surface. The sample for micro CT was glued using epoxy resin onto a massive steel disk with a 5 mm high skirting. Skirting is used to keep the fluid level above the sample’s surface during nanoindentation measurements under the various fluids tested here. The sample is kept inside the nanoindentation system under a controlled environment (temperature +22.5°C, 60% humidity) for...
48 h to allow for solidification of epoxy, relaxation of stresses induced during sample preparation, and evaporation and/or equilibration of residual water inside the sample.

The X-Y-Z stage of the nanoindentation system is mechanically synchronized with an optical microscope with an accuracy of about 1 μm, allowing the indentation at a precise point on the surface. As the sample surface is visualized through optical microscopy, up to 1000 points on the surface are selected for measurements during one automated run of the experiment. The number of measurement points have been selected in two ways: 1) creating a rectangular fixed step grid approximately 3 mm by 3 mm (33 rows by 33 columns) on a sample, this method of point selection is similar to the grid-indentation technique used for example by Ortega et al. (2007), or 2) visually defined by an operator (640 measured points are shown as black dots in Figure 4). Regardless of the method of point selection, for each indented surface point a corresponding indentation modulus is estimated. It takes about 36 hours to complete 1000 measurements on the sample. The inset in Figure 5(a) shows a photograph of the indenter during measurements on a dry sample.

After performing measurements on a dry sample, distilled water is directly applied to the sample’s surface and the sample is kept submerged for 48 h to ensure saturation. It was verified that water has fully penetrated inside the sample due to gravity and capillary forces based on observations in micro CT experiments, which we will not elaborate on here. In addition, the upper 1 mm layer of the sample is uniformly saturated without any trace of air (100% water saturation). The nanoindentation measurements are repeated on a water-saturated sample. However, in this case all points have been shifted by 10 μm to perform measurements on the “intact” surface. In the water-saturated experiment, the indentation is done through an approximately 5 mm covering layer of water. A water-covering layer had no effect on measurement results for the “standard” materials when compared with their dry state. A photograph of the indenter immersed into water is shown in the inset in Figure 5(b).

Excess water was removed from the surface and the sample dried inside the apparatus by a hot air gun for 4 hours and then kept for 48 hours at a constant +22.5°C and 60% humidity to return the sample to the same environment as for the first measurements (i.e. a dry sample).
locations of all measurement points were shifted again by 10 μm and new measurements were taken. The sample was then saturated with an alkane hydrocarbon (C_{10}H_{22}, n-Decane), and left to equilibrate for 24 hours. Indentation measurements were repeated under a 5 mm fluid covering layer of the alkane hydrocarbon.

For all measurements, the maximum load of the indenter was fixed at the level of 10 mN (1.02 gf). Raw data was screened manually and unrealistic load vs depth records (about 5% of total number of measurements) were removed from the following analysis. “Initial penetration” and “area function” corrections have been applied for all data prior
to calculations of the indentation modulus using internal software.

To evaluate the changes of the elastic moduli at a large scale, the same steps of fluid saturation (dry, water, dry, n-Decane) are repeated with the bigger plug of the Savonnières sample (diameter – 38.55 mm, length – 70.05 mm; He-gas porosity – 30.5 %, permeability – 61 mD). Fluid saturation was performed by vacuuming the sample under stress inside a pressure cell and following flooding with pressurized distilled water or n-Decane. Ultrasonic P-wave ($V_p$) and S-wave ($V_s$) velocities are measured at room conditions. The details of the experimental set-up for ultrasonic measurements is described in Lebedev et al. (2013). Shear ($\mu$) and Young’s ($Y$) moduli are calculated using the following formula:

$$\mu = \rho V_p^2,$$

$$Y = \frac{\rho V_p^2(3V_p^2 - 4V_s^2)}{V_p^2 - 2V_s^2},$$

where $\rho$ is the density of the sample.

RESULTS

Figure 5 shows the cumulative distribution of indentation moduli measured at 649 points on the exact same area (3 mm x 3 mm) for a dry (Figure 5(a) and water-saturated (Figure 5(b)) sample. It can be seen from this figure that the indentation modulus distribution for the wet sample is shifted to lower values when compared with the modulus distribution obtained for the dry sample. The estimated Voigt-Reuss-Hill average indentation modulus (weighted by frequency) for this area in dry and water saturated conditions are 32.0 GPa, and 30.2 GPa, respectively.

The distribution of the indentation moduli for dry, water saturated, dried after water saturation, and saturated with n-Decane conditions is shown in Figure 6. The decrease of the indentation modulus due to water interaction with the rock sample is again confirmed. After drying the sample, the indentation modulus increases but does not exactly match the initial state of the starting dry sample. No remarkable difference in moduli distributions is observed between the dried (stage 3) and n-decane saturated sample (stage 4).

To understand which elements of the rock are affected by water, the points of the indentation were chosen according to the map shown in Figure 4. The results of experiments were grouped by particular areas on the sample, such as different ooids cortices, pore occluding prismatic cement, intra-ooid porosity and intergranular porosity, and are shown in Figure 7. Water weakening can be mainly observed for the peloid nuclei, prismatic cements partially infilling intergranular porosity as well as for ooid cortices. No remarkable changes in the indentation modulus for the central parts, including the peloidal sediment infills and the intragranular porosity within ooids, is observed.

Ultrasonic measurements of P- and S-wave velocities performed at ambient conditions on a cylindrical core of Savonnieres limestone for dry, water saturated and n-Decane saturated conditions show a shear modulus reduction for water saturated samples from 8.35 GPa (dry) to 7.65 GPa (water saturated) and a subsequent increase up to 8.27 GPa (n-Decane). However, based on ultrasonic measurements, the Young’s modulus of this sample measured in dry and water saturated and n-decane saturated conditions remains practically unchanged at 20.4 GPa, 20.3 GPa, and 20.3 GPa, respectively.

DISCUSSION

Nanoindentation experiments

The nanoindentation technique is an emerging technique in rock physics. The experimental protocol applicable for complicated rock samples is not well developed yet, thus in our experiments significant efforts were spent on the development and validation of the experimental procedure.

On a sub-millimetre scale, the Savonnieres limestone is a highly inhomogeneous sample. The distribution of the indentation modulus is broad, thus it is important to find out how many measurement points are necessary to obtain statistically valid results. To evaluate statistical validity, three indentation experiments were performed with 1000, 340 and 100 measurement points each on the same area of Savonnieres limestone. The results are presented in Figure 8; modulus distributions obtained from 1000 and 340 points are similar to each other, however, the distribution obtained using 100 points is notably different. Thus, for the main series of experiments at least at 300 points were measured. If, however, the indentation was done on a more uniform area of rock for which the modulus distribution is not broad, the limit of the minimum number of measured points may be decreased to 100.

In nanoindentation experiments there are several factors influencing the final results. Sample preparation and sample fixation onto a substrate is an important procedure in this technique. The surface of the sample should be as flat as
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possible to avoid the influence of surface roughness on the indenter’s tip. The sample should be fixed firmly onto a rigid holder. The selection of measurement parameters such as maximum force, rate of loading and unloading, and distance between measurement points, should be chosen in such a way that mechanical damage to the substrate in the vicinity of the current measurement point (which is unavoidable) does not affect the conditions of the substrate in the following points. In our experiment, the average maximum penetration of the indenter is about 0.6 μm, and the maximum area of contact between the indenter and sample estimated from equation (2) is 8.8 μm², taking into account that the maximum load is 10 mN. The maximum stress at the area of contact of the indenter and substrate is about 1.1 GPa. This high stress induces plastic deformation and some damage of the sample in the vicinity of the measurement point. From finite element method (FEM) simulations (Torres-Torres et al. 2010) the stress decreases by three orders of magnitude (to 1 MPa) at a distance of 11.3 μm from the measurement point. It therefore seems reasonable to assume that to avoid the influence of substrate damage from the current measurement point on the following measurements, the steps between acquisition points should exceed 10 μm. Such safety distance between measurement points was experimentally confirmed by four consecutively tests on a dry Savonnières rock sample. The same grid was used in each test but all measurement points were shifted by 10 μm from the position in previous measurements. All four tests show the same modulus distribution.

Another conclusion following from the above estimations is that the indentation modulus is measured not at a small point but for a relatively large volume of about 10³ μm³. This means that neighbouring elements in the rock may affect the measurements. The indentation modulus for the area inside the grain will be different from that close to a grain boundary (even for a homogeneous grain), as the grain is bonded to other grains and such bonding may decrease or increase rigidity of the grain.

The sample is firmly fixed (epoxy-glued) on the sample holder to avoid any bending during measurements. To eliminate the influence of the sample holder, the thickness of the sample was at least 100 times higher than maximum penetration depth (Lebedev and Krumdieck 2008).

Causes of Weakening of the Savonnières limestone

The Savonnières limestone sample is mainly composed from calcite (CaCO₃), which has a low solubility in distilled water (14 mg/L) (Haynes 2013). After contact with the atmosphere in a laboratory room, water absorbs carbon dioxide and as a result the solubility of calcite increases up to 47mg/L (Haynes 2013).
Figure 7 Distribution of indentation modulus for: (a) Bladed cement partially infilling intergranular porosity; (b) Peloid nucleus to ooid; (c, h) Intra-ooid porosity after dissolution of the nucleus; (d, g) Ooid cortex; (e) peloidal sediment infill of ooid; (f) peloidal sediment infill of superficial ooid under dry and wet conditions: Red colour – dry, Blue-water-saturated sample. The areas of measurements are shown as green filled areas in the embedded optical image. For each area the measurements are performed on 100 points. All measurements points are shown in Figure 4.
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Figure 8 Indentation modulus distribution dependence on number of measurement points on the same area 1 mm x 1 mm of Savonnières limestone: (a) 1000 measurement points, distance between points 31 μm; (b) 340 points, distance between points 58 μm; (c) 100 points, distance between points 110 μm.

2013). The simplified equation for calcite solubility with CO₂ and water can be written as:

\[ \text{CaCO}_3(s) + \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ca}^{2+} (aq) + 2\text{HCO}_3^- (aq). \]

Our experimental observations show that after drying the water-saturated sample, the indentation modulus (Figure 6 graph 3) does not return to the initial dry state (Figure 6 graph 1). This data indicates that the sample microstructure was altered by being in contact with distilled water. Parts of the sample have either been dissolved or mechanically compacted and then may have even been affected by mineral precipitation after the drying process.

From Figure 7 we can observe the decrease in indentation modulus due to interaction with water for cement between oolite grains, peloid nuclei and for ooid cortex areas. The other parts of the sample do not show significant changes in indentation modulus. The Savonnières limestone is widely used as a building stone and in other studies the palisadic cements were found to be much less prone to alteration or dissolution than the ooid cortices (Fronteau et al., 2010). It is possible that the decrease in indentation modulus observed after water saturation of the palisadic cements in fact represents their compaction into partially dissolved ooid cortices or into areas of biomoldic porosity where the pre-existing micrite envelope supporting some palisadic cements has been weakened by dissolution.

Conclusions and Future work

The nanoindentation method was successfully applied for evaluating changes in the mechanical properties due to rock-water interaction at the micro-scale level. The experiments carried out for the dried, water-saturated, and hydrocarbon-saturated Savonnières limestone demonstrated a decrease in the elastic modulus of a water-saturated sample. By precisely controlling the measurement area in the nanoindentation experiments it was demonstrated that the palisadic cement partially infilling intergranular porosity, as well as the peloidal nuclei and ooid cortices are mostly affected by introducing distilled water. We interpret that the reason for the decrease in elastic modulus is partially due to dissolution of calcite and/or compaction into voids or ooid cortices for the cements. No significant change in elastic modulus was observed when hydrocarbon (n-decane) saturated the sample. The weakening of the solid matrix of Savonnières limestone found in our indentation experiments was confirmed by a decrease in the samples' shear modulus measured at ultrasonic frequency.

Solubility of calcite drastically increases with increasing amounts of CO₂ dissolved in water and/or increasing the salinity of brine. Results presented in this paper with distilled water will be used as a reference in our future experiments in which we will investigate the influence of brine, brines chemically equilibrated with a “chunk” of carbonate and brine with dissolved CO₂ on the mechanical properties of carbonates. Control of chemical reactions that occur and measurement of pH of fluid before and after flooding, will be an essential part of the future study.
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