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1 The effect of CO₂-enriched brine injection on the mechanical properties of calcite-bearing
2 sandstone.

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9 Abstract

10 The mechanical and fluid-flow response of subsurface geological reservoirs due to injection
11 of CO₂ is of critical importance for the safe management and storage of anthropogenic carbon
12 emissions. Although the time-lapse seismic method has proven to be an effective tool to
13 remotely monitor changes in underground fluid saturations, variations in reservoir properties
14 caused by geochemical interactions can also influence the seismic response. This can lead to
15 ambiguity and uncertainty in monitoring the movement of injected CO₂ and hence
16 determination of reservoir seal integrity. Geochemical interactions can also modify the
17 mechanical strength of the reservoir and therefore threaten its integrity. We conducted
18 experiments to assess how the velocity and rock strength of a calcite-bearing sandstone are
19 affected by flooding with CO₂ saturated brine. The results indicate that both seismic velocity
20 and rock strength are significantly reduced due to minor calcite dissolution. The implications
21 at the reservoir scale for CO₂ storage are twofold. Firstly, modifications in velocity can
22 complicate seismic monitoring operations and lead to interpretation errors. This can be

23 accounted for if shear wave velocity variations are used to detect fluid-rock interactions.
24 Secondly, reduction in rock strength, caused by calcite dissolution, can threaten reservoir and
25 wellbore integrity under stress conditions typically found in potential carbon repositories.

26 Keywords.

27 Carbon storage, Fluid-rock interactions, Yield stress, Sonic velocity

28 1. Introduction

29 Monitoring CO₂ injection is an essential component of the geological carbon storage (GCS)
30 chain as it can condition public acceptance and will likely be necessary to comply with
31 regulations. Time-lapse seismic methods have generally been considered to be a sufficiently
32 accurate means of monitoring CO₂ saturation in the subsurface in terms of both the flow and
33 the storage of injected CO₂ for various GCS pilot studies (Cook, 2014; White, 2013;
34 Chadwick et al., 2010; Daley et al., 2008). To increase the confidence in this method it is
35 essential to understand how geochemical interactions triggered by CO₂ injection modify the
36 mechanical response of the reservoir and surrounding rocks (Vanorio et al., 2011; Hangx et
37 al., 2013; Clark and Vanorio, 2016). Rock sonic velocity has a directly influence on seismic
38 imaging while rock deformation can also lead to noticeable effects in time-lapse seismic
39 analysis (e.g., Herwanger and Koutsabeloulis, 2011). Rock mechanical properties also
40 influence the injection operations by constraining the maximum safe injection pressure and
41 controlling fault reactivation, reservoir deformation and in turn wellbore and caprock
42 integrity. Consequently, we focus on two properties of interest which are the rock seismic
43 velocity and the rock strength.

44 In saline aquifers repositories, CO₂ dissolution in brine can lead to brine acidification, one
45 direct consequence is the dissolution of carbonate minerals and hence a modification of the
46 rock framework and mechanical behaviour. Vanorio et al. (2011) studied salt precipitation

47 and carbonate dissolution effects in limestone and concluded that they were significant for
48 modelling and interpreting time-lapse seismic signals. The hypothesis that geochemical
49 effects could be significant is appealing since it could explain some inconsistencies between
50 measured and predicted velocities that have been observed at various GCS sites. For example,
51 a larger than expected velocity slowdown was observed at Frio (Daley et al., 2008). In
52 particular, the S wave velocity decrease could indicate a change in the rock frame as this
53 parameter is supposedly insensitive to changes in pore fluids. Hangx et al. (2013) found that
54 sonic velocity and rock strength were not significantly affected by small amounts of carbonate
55 dissolution because the rock was quite quartz cemented. They concluded that “for less quartz-
56 cemented sandstones there may be an increased risk for calcite-dissolution-induced
57 weakening”.

58 In this paper, experimental results obtained from rock cores of a sandstone collected from
59 Cayton Bay, NE England, are used to illustrate the effects of calcite dissolution triggered by
60 reaction with CO₂ on sonic velocity and mechanical properties. Minor amount of calcite
61 dissolution has already been shown to significantly enhance the permeability of the Cayton
62 Bay sandstone (Lamy-Chappuis et al., 2014). In the current study, a flow through reactor
63 apparatus was used to dissolve calcite from cores that were then subjected to series of sonic
64 velocity and strength measurements. The comparison with baseline values revealed a
65 significant reduction in sonic velocity and strength. The consequences for GCS management
66 need to be discussed.

67 2. Sonic velocity

68 2.1 Sonic velocity usage and limitations for GCS

69 Sonic velocity data is routinely used to quantify fluid saturation, porosity and the lithology of
70 underground reservoirs (Sheriff and Geldart, 1995). Time-lapse seismic monitoring is the

71 most relevant technique to track changes in fluid distributions during reservoir production
72 (Calvert, 2005), it is based on the interpretation of changes in seismic properties (e.g.,
73 reflection, travel-times and amplitudes). This technology is viewed as an essential tool to
74 monitor fluid injection and fluid flow for GCS projects (Chapman et al., 2000; Arts et al.,
75 2004; Brown et al., 2002; Li, 2003). It is also thought that detailed interpretation of time-lapse
76 seismic data could provide pore pressure information (Grude et al., 2013, White et al., 2015).

77 Traditionally, changes in seismic response may primarily be attributed to saturation changes
78 due to fluid substitution stemming from CO₂ injection. The effect of fluid substitution can be
79 modelled using the Gassmann and Biot equations (Gassmann, 1951; Biot, 1956a, b; Mavko
80 and Jizba, 1991; Han and Batzle, 2004). By default, these equations do not address the effects
81 of geochemical interactions on the rock frame behaviour, which could lead to interpretation
82 errors. This is important because it has been recognized that the elastic behaviour of rock is
83 nonlinearly dependent on stress (Walsh, 1965a, 1965b; Nur and Simmons, 1969) and so any
84 modifications of the mechanical strength of the rock can influence the stress dependent
85 behaviour (Verdon et al. 2008). In addition, geochemical interactions could lead to changes in
86 mechanical strength and to deformation manifested in time-lapse seismic effects (e.g.,
87 Herwanger and Koutsabeloulis, 2011). It is therefore useful to compare the impacts of fluid
88 substitution and calcite dissolution on sonic velocity.

89 2.2 Experimental design

90 The experimental setup consisted of a triaxial cell instrumented for ultrasonic velocity
91 measurement under variable pressure and fluid saturation conditions (Figure 1). The vertical
92 press was programmed to perform an axial loading and unloading cycle while the lateral
93 pressure was manually controlled with an external pump to maintain isostatic conditions.
94 Experiments were done at a temperature of 50±2°C (above the critical temperature of CO₂).

95 Piezoelectric transducers mounted at the ends of steel platens were used to generate a 1 MHz
96 P wave and two 0.7 MHz orthogonally polarized S waves to measure a fast and slow shear
97 wave. A disk of lead foil was placed in either end of the sample to improve the contact
98 between the transducers and the cores. Travel times were determined for the first peaks
99 corresponding to the sonic wave's arrivals and were zeroed by doing a measurement with no
100 rock core. The difference in orthogonal S waves velocities at any fluid saturation conditions
101 never exceeded 0.3%, meaning that the rock cores were fairly isotropic. For simplicity, in the
102 remainder of this paper the average S wave velocity is reported.

103 Rock cores were drilled with a diameter of 3.75 cm, carefully cut to a length of 7.30-7.80 cm,
104 with special care to ensure that the ends were perfectly perpendicular to the axis of the core
105 plugs. The cores were then dried in an oven for 48 h at 60°C. The samples were then left dry
106 or saturated with CO₂ or brine under vacuum, the saturating fluids would then be pressurized
107 with an external ISCO pump and heated in a core holder. All experiments were done in
108 drained conditions (i.e. fluids were allowed to move in and out of the sample).

109 Pressure conditions were chosen to span a large range of relevant in-situ reservoir conditions.
110 The pore pressure was varied between 3.4 and 27.5 MPa. Lateral confining pressure and axial
111 load were varied between 6.9 and 69 MPa and were kept isostatic. The resulting effective
112 pressure for each experiment ranged between 3.5 and 41.5MPa (effective pressure = confining
113 pressure - pore pressure). Various experimental conditions were used to examine the effect of
114 fluids, fluid pressure and calcite dissolution on the sonic velocity, see Table 1.

115 2.3 Results

116 2.3.1 Rock and fluid controls on velocity

117 A preliminary series of measurements was done on unaltered samples to evaluate the effect of
118 effective stress, pore pressure and fluid composition (either 1M NaCl brine or CO₂) on sonic
119 velocity, this experiment serves as a base case where geochemical interactions are neglected.

120 Figure 2 presents sonic velocity data obtained on one core (core number 3.1) at varying
121 effective stress conditions imposed by a confining pressure loading and unloading cycle (the
122 pore pressure is kept constant during each cycle). There is a clear influence of the effective
123 pressure on the sonic velocity that shows a consistent increase with effective stress at all fluid
124 saturation conditions. The velocities tend to converge at the maximum confining/effective
125 pressures, this is generally attributed to micro-cracks and compliant pores closing within
126 increasing stress and to interactions at the grain boundaries. This effect is reversible since the
127 velocity curves are almost the identical during the loading and unloading paths. The low
128 amount of hysteresis is a good indication that the samples were not damaged during loading
129 and thus could be re-used for further experiments.

130 S wave velocity (V_s) decreases gradually with increasing CO₂ pressure (i.e. with increasing
131 CO₂ density). Brine saturated samples have the lowest velocities, which is consistent with
132 brine having the highest density at all studied pressures. Brine being incompressible, the sonic
133 velocity in the brine-saturated case does not depend on fluid pressure (for a given effective
134 pressure). The pattern is different for the V_p where the slowdown does not exactly follow the
135 density trend. This difference is due to brine having a bulk modulus that is several orders of
136 magnitude larger than that of CO₂ and this partly counterbalances the effect of density on the
137 velocity. As a result, the V_p/V_s ratio is significantly higher when the rock is brine saturated
138 and this is known to be a very good indicator of the type of fluid substitution. Overall it is

139 clear that the changes in fluid density dominate the differences in velocities for this
140 experiment. In particular, the observed velocities under fluid saturated conditions are lower
141 than in the dry case and are consistent with Gassmann equation calculations (see Appendix B)
142 where we only took into account density variations and neglected high frequency viscous
143 effects (i.e. squirt flow). There is however a general overestimation of the velocities
144 calculated with Gassmann equations, especially (but not limited to) the brine-saturated cores.
145 This fall within the uncertainty of the Gassmann equation input parameters but could also
146 point towards a secondary effect affecting the experimental results. One possibility is that the
147 dry cores were “over-dried” leading to an overestimation of the dry cores bulk modulus which
148 is used in Gassmann equation to calculate the sonic velocity of the fluid-saturated rock. The
149 other possibility is that the fluids have a “lubrication” effect whereby the rock frame is
150 weakened and produce anomalously low S and P waves velocities. This is consistent with the
151 brine-saturated measurements being particularly affected since brine has a much higher
152 wettability than CO₂ at our experimental conditions.

153 2.3.2 Impact of calcite dissolution on sonic velocity

154 Four experiments have been conducted on dry cores (cores 2.1, 3.1, 3.2 and 4.1) to evaluate
155 the change in sonic velocity after calcite dissolution. We used only dry cores in order to
156 suppress the possibility of ambiguous interpretation caused by the introduction of fluids and
157 because this is relevant to common industry practice whereby the properties of fluid-saturated
158 rocks are predicted from their dry counterpart using Gassmann equations. As previously
159 described in Lamy-Chappuis et al. (2014), the Cayton Bay sandstone contains dispersed shell
160 fragments accounting for about 5% of the grain volume (Figure 3) and their dissolution has
161 already been shown to have a rapid and significant effect on transport properties. No other
162 significant geochemical reactions were recorded. In particular, clays, which are known to
163 affect sonic velocity, were unaffected by CO₂-saturated brine flooding (Lamy-Chappuis et al.,

164 2014). For each core, the porosity was recorded before and after total calcite dissolution using
165 helium porosimetry. Sonic velocity measurements done before and after calcite removal are
166 shown in Figure 4.

167 The main features of Figure 4 are the large variability in initial sonic velocities and the
168 significant velocity slowdown after calcite dissolution for all cores. A striking observation is
169 that the decrease in velocity is comparable to the one caused by fluid substitution (as shown in
170 Figure 2), roughly $10 \pm 5\%$ decrease depending on the porosity change. This slowdown
171 applied to V_P and V_S in a similar fashion so that the V_P/V_S ratio was left relatively unchanged.

172 Eq. (1) was used to calculate the bulk and shear moduli from sonic velocity data, before and
173 after calcite dissolution.

$$174 \quad K_{dry} = \rho \left(V_P^2 - \frac{4}{3} V_S^2 \right) \text{ and } M_{dry} = \rho V_S^2, \quad (1)$$

175 where K_{dry} is the dry rock bulk modulus, M_{dry} is the dry rock shear modulus and ρ is the
176 rock density.

177 Figure 5 reveals that both parameters were reduced to an average of 80% of their initial value
178 and the dissolution effect is quite insensitive to the effective pressure conditions. This means
179 that the pores created by calcite dissolution were not significantly more or less compliant than
180 the original pores. Also, calcite dissolution did not modify the stress sensitivity of the
181 poroelastic response as could be the case if calcite was found as a cement (rather than as
182 isolated fragments) or at grain boundaries.

183 The velocity is in fact closely correlated to the absolute porosity value. The natural porosity
184 variation and the one caused by calcite dissolution produces the same trends when plotting
185 velocities against porosity (Figure 6). This supports the idea that for a given rock texture the
186 absolute porosity is the primary variable upon which sonic velocity depends. This is the idea

187 behind classical velocity-porosity correlations such as the Wyllie time average equation or
188 more advanced empirical correlations (Raymer et al., 1980; Han et al., 1986; Tosaya and Nur,
189 1982; Castagna et al., 1985).

190 The experimental correlation from Han is very accurate in term of absolute velocity prediction
191 based solely on porosity and clay content although the velocity gradient with porosity is lower
192 than in the present experiments. Other correlations obtained on water-saturated samples (e.g,
193 Tosaya and Castagna correlations) unsurprisingly do not predict the absolute “dry” velocities
194 but are better at predicting the relative slowdown caused by calcite dissolution (Figure 7). All
195 the equations for these correlations can be found in Mavko et al. (2009) and in Appendix A.

196 2.3.3 Significance for time-lapse seismic monitoring of GCS

197 By using the experimental data it is possible to construct a CO₂ injection scenario and identify
198 the best indicators for tracking fluid substitution and calcite dissolution. Figure 8 shows a
199 possible time sequence (from left to right). The initial reservoir state (left column) is 100%
200 brine saturation with a pore pressure of 14 MPa and an effective pressure of 14 MPa. The
201 second stage (second column from left) retains the same fluid saturation but the brine pore
202 pressure has been increased to 21 MPa and hence a reduction in effective pressure to 7 MPa.
203 In the third stage (third column from left) the brine has been fully replaced by CO₂ at the
204 same pore pressure of 21 MPa. The last stage (column on the right) is an end-member case
205 including both fluid substitution and calcite dissolution effects (i.e., reduction of mechanical
206 strength) on the velocities. Note that in the figure, all velocities are normalized to an initial
207 velocity, which value as been arbitrarily set to 100.

208 For the P wave velocity, the change in fluid pressure has a small effect. However, fluid
209 substitution reduces the velocity by roughly 10% and calcite dissolution reduces the velocity
210 by another 10%. For the same sequence of stages, the only significant change in S wave

211 velocity is due to calcite dissolution (about 10% decrease). The ratio V_P/V_S is essentially
212 constant during reservoir pressurization and calcite dissolution, yet is strongly sensitive to
213 fluid substitution. The results of this analysis suggests that V_P/V_S should be used to detect
214 replacement of formation water by CO_2 and V_S alone should be used to detect changes in the
215 rock frame due to mineral dissolution.

216 Only considering V_P during time-lapse seismic analysis could lead to large interpretation
217 errors. Figure 9 shows the evolution of the P wave velocity with fluid substitution calculated
218 with Gassmann equations (see Appendix B). The bulk modulus of the brine- CO_2 mixture was
219 calculated with Wood's equation (Wood, 1941). For the "Normal fluid substitution" curve
220 only the CO_2 saturation was varied. For the "Fluid substitution and increase in porosity" curve
221 the fluid rock interactions were incorrectly taken into account by simply increasing the
222 porosity parameter in Gassmann equation. The last curve is the most accurate as it takes into
223 account fluid-rock interaction effects on both porosity and K_{dry} parameters (as evaluated in
224 the present experiments, details can be found in Appendix B).

225 It appears that a few percent of CO_2 saturation associated with calcite dissolution (lower
226 curve) could be misinterpreted as 100% CO_2 infiltration with no proper account of calcite
227 dissolution (upper curves). In practice the true V_P -saturation curve will lie between the two
228 end-member curves as calcite dissolution and CO_2 invasion happen simultaneously.

229 This indicates that a detailed analysis of the sonic velocity changes is recommended to
230 discriminate between the effects of fluid substitution and rock frame modification. Detailed
231 velocity analysis may not necessary if the purpose of time-lapse monitoring is simply
232 intended to detect CO_2 leaks into the overlying geological layers. However, detailed analysis
233 is recommended if the purpose of time-lapse monitoring is to track accurately the CO_2
234 propagation or quantify localized fluid-rock interactions in the reservoir and in the

235 surrounding layers. Localization and quantification of rock frame modifications could be
236 useful to monitor and prevent reservoir and wellbore deformation (Kristiansen and Plischke,
237 2010). In this framework, the following section addresses the consequences of calcite
238 dissolution for the strength of the Cayton Bay sandstone. It is important to know if, for a
239 given reservoir stress state, geochemical reactions can significantly weaken the rock and
240 consequently lead to rock yielding or failure. Yielding or failure could compromise both
241 wellbore and formation stability as well as reduce the reservoir permeability.

242 3 Peak and yield strength

243 3.1 Experimental design

244 Multiple failure experiments were used to obtain peak and yield stress data points at
245 increasing confining pressures. The experiment proceeds as series of single failure tests where
246 the confining pressure is quickly increased to reestablish isostatic pressure when the sample
247 starts to fail. Usually strength results obtained from multistage tests are systematically lower
248 than results from single-stage tests because the sample gets weaker as it becomes slightly
249 damaged by incipient yielding and fracturing at each stage. This technique is, however, less
250 time consuming and works very well on relatively plastic rocks where failure does not occur
251 dramatically and confining pressure can be increased on time. It also removes issues
252 regarding sample heterogeneity compared to when the failure envelop is measured based on
253 multiple single-failure experiments.

254 Initial tests on Cayton Bay sandstone indicated that the multiple failure test was well suited to
255 this rock, which is quite plastic under the stress conditions used. Two separate sets of cores
256 were used, one unreacted and the other one where the calcite had been dissolved. Nine
257 multiple failure test were conducted on water saturated cores in drained conditions and at
258 room temperature.

259 A triaxial testing machine was equipped with LVDT (Linear Variable Displacement
260 Transducer) to record the axial strain. The LVDT result from one experiment is shown in
261 Figure 10. After each confining pressure increase, axial unloading and reloading cycle was
262 performed, allowing the rock to return into the elastic domain.

263 The yield points are defined as the points where the curve departs from the linear elastic trend.
264 The confining pressure was increased in seven stages at 5, 10, 20, 30, 40, 50 and 60 MPa.
265 After the last stage was reached the confining pressure was gradually reduced to evaluate the
266 residual strength of the rock. In general, the onset of rock failure occurred at 10MPa above the
267 yield point.

268 3.2 Calcite dissolution effect on rock strength

269 The yield stress envelope created by plotting all yield points on a σ_1 - σ_3 plot (Figure 11)
270 shows that calcite dissolution effectively decreased the strength of the rock.

271 For illustration the σ_1 - σ_3 state for a hypothetical reservoir where faults with a friction
272 coefficient of 0.85 constrain the stress state is shown in Figure 11. The calculation used a
273 continuous underground rock density of 2800 kg.m^{-3} , which represents a hypothetical average
274 density of rocks situated above a layer of Cayton bay sandstone, and assumed that the pore
275 pressure was hydrostatic. Three points are shown, corresponding to the state in the reservoir at
276 depths of 1000, 2000 and 3000m. In the ideal case, (Jaeger and Cook, 1979) the ratio of
277 $\sigma_1 - P_f$ to $\sigma_3 - P_f$ is a function of the fault friction coefficient μ as follows:

$$278 \frac{\sigma_1 - P_f}{\sigma_3 - P_f} = \left(\sqrt{\mu^2 + 1} + \mu \right)^2 \quad (2)$$

279 where P_f is the pore pressure. For a normal faulting regime σ_1 is the vertical stress, equal to
280 $\rho g z$, then at 1000 m $\sigma_1 - P_f = 18 \text{ MPa}$ and $\sigma_3 - P_f = 4 \text{ MPa}$. Similarly for 2000 m $\sigma_1 - P_f =$
281 36 MPa and $\sigma_3 - P_f = 8 \text{ MPa}$; for 3000 m, $\sigma_1 - P_f = 54 \text{ MPa}$ and $\sigma_3 - P_f = 12 \text{ MPa}$.

282 The curves in Figure 11 indicate that it is possible for calcite dissolution to trigger ductile
283 yielding in the hypothetical reservoir at a depth of about 2000 m, at this depth the yield stress
284 of the reacted samples are all inferior to the reservoir principal stress. At 1000 m none of the
285 samples would yield while at 3000m only two unreacted samples would not yield.

286 The decrease in rock strength is likely due to a decrease in rock cohesion and in the angle of
287 internal friction. Rewriting the Coulomb law of failure as:

$$288 \quad \sigma_1 = \frac{2\tau_0 \cos \varphi}{1 - \sin \varphi} + \sigma_3 \frac{1 + \sin \varphi}{1 - \sin \varphi} \quad (3)$$

289 where τ_0 is the rock cohesion and φ is the angle of internal friction; linear fits to average peak
290 envelopes before and after calcite dissolution (Figure 12) translates into τ_0 decreasing from
291 14.5 to 10.5 MPa and φ decreasing from 16.0 to 8.3°.

292 On Figure 10 there is no clear break between results for reacted and unreacted cores. The
293 yield stress curves are shown as a function of porosity in Figure 13. These results suggest that
294 the decrease in strength is a strong function of porosity, irrespective of whether it is original
295 or secondary. This result is analogous to the one obtained on sonic velocity.

296 4. Conclusion

297 The experimental results presented here provide very strong evidence that fluid rock
298 interactions cannot be neglected when dealing with the mechanical properties of calcite
299 bearing reservoirs in the context of GCS. They show large modifications of the sonic velocity
300 and rock strength parameters upon calcite dissolution. For instance, this study shows that a
301 10% porosity increase can provoke a 10% decrease in sonic velocity which is the same order
302 of magnitude as the velocity decrease expected during fluid substitution from brine to
303 supercritical CO₂.

304 The results show that a good first order prediction of the velocity change upon calcite
305 dissolution can be achieved by using simple correlations found in the literature. Care should
306 be taken before generalizing this result since this study only examined the effect of a small
307 amount of calcite dissolution in the form of isolated shell fragments. It is also worth noting
308 that these fragments had similar sizes to the pre-existing pores (approximately 100 μm
309 diameter). It is possible that different sandstone textures would produce different results
310 depending on the nature of the reactive minerals, their proportion in the rock and their
311 placement in the rock frame.

312 At the reservoir scale the possible implications of this study are twofold. Firstly, the work
313 conducted on sonic velocity demonstrates the fluid-rock reactions must be accounted for to
314 properly interpret seismic data in terms of fluid saturation. Secondly the study of the yield and
315 peak envelopes demonstrates that fluid-rock interactions can in some circumstances be a
316 threat to reservoir and/or well integrity by reducing rock strength and triggering irreversible
317 plastic deformation. However, rock compaction after yielding could mitigate this effect by
318 increasing rock strength. The exact implications of this work at the reservoir scale will depend
319 on the extent and localization of calcite dissolution.

320 The changes in porosity and rock properties associated with fluid-rock reactions could be
321 calculated and localized with time-lapse seismic surveys of P and S wave components. This
322 could provide a means to assess the reservoir and well instability risk and would necessitate
323 an integrated reservoir mechanical modelling that is out of the scope of this study.

324 The correlation between porosity and rock mechanical properties is very strong in these
325 experiments, such that the effect of natural porosity variations is almost independent of
326 whether porosity is original or created experimentally by calcite dissolution. This conclusion
327 is very different from the one reached for the transport properties in Lamy-Chappuis et al.
328 (2014). In their study of the Cayton Bay sandstone, the changes in transport properties

329 depended on the change in pore network morphology rather than on the absolute change in
330 pore volume, this is the opposite for the sonic velocity and rock strength properties.
331 Nevertheless, it is not possible to generalize this result to all calcite bearing sandstones as it
332 seems logical that in some conditions the pore morphology would have a larger influence.

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338 I. Appendix A

339 Details of empirical sonic velocity-porosity correlations used for Figures 6 and 7.

340 Raymer: $V_p = 5800 (1 - \theta)^2 \text{ m/s}$

341 Han: $V_p = 5410 - 6350 \theta - 2870 c \text{ m/s}$

342 $V_s = 3570 - 4570 \theta - 1830 c \text{ m/s}$

343 Tosaya: $V_p = 5800 - 8600 \theta - 2400 c \text{ m/s}$

344 Castagna: $V_p = 5810 - 9420 \theta - 2210 c \text{ m/s}$

345 All equations are applicable for the Cayton Bay sandstone which has a porosity θ of 30% and
346 a clay content c of 5%.

347 II. Appendix B

348 The Gassmann equation has been used to predict the change in sonic velocity caused by
349 changes in fluid saturation. According to these equations the bulk and shear moduli of a fluid
350 saturated rock can be calculated with the separate mechanical properties of the dry rock and
351 fluid:

$$352 \quad K_{sat} = K_{dry} + \frac{\left(1 - \frac{K_{dry}}{K_m}\right)^2}{\frac{\phi}{K_{fl}} + \frac{1-\phi}{K_m} - \frac{K_{dry}}{K_m^2}}$$

$$353 \quad M_{sat} = M_{dry}, \quad (B1)$$

354 where K_{sat} , K_{dry} , K_m , and K_{fl} are the bulk moduli of the saturated rock, dry rock, mineral
355 composing the rock and saturating fluid respectively; M_{sat} and M_{dry} are the shear moduli of
356 the saturated and dry rock; ϕ is the rock porosity. This equation allows the estimation of
357 seismic velocities of rocks saturated with various fluids when knowing dry rock velocities.

358 Figure 9 calculation of the fluid substitution curve accurately including calcite dissolution
359 effects:

360 For K_{dry} the experimental data obtained on sample 3.1 was employed (this experiment
361 produced an intermediate reduction of K_{dry} by about 20%) , K_m was calculated using the
362 Voight-Reuss-Hill average (Hill, 1952) from the data shown in table B1.

363 K_{fl} for CO₂ and brine were calculated from speed of sound equations of Span and Wagner
364 (1996) and Batzle and Wang (1992) for CO₂ and brine respectively. For the Gassmann
365 modelling the rock density was taken as 1780 kg/m³, porosity as 32.5% and K_m as 34.5 MPa
366 (these are averages over all Cayton Bay rock cores); other parameters used for the modelling
367 are shown in table B2. The shear modulus of the fluid-rock system is assumed to be equal to

368 that of the dry rock frame since CO₂ and brine have no shear strength under liquid and
369 supercritical conditions, see Eq. (B1).

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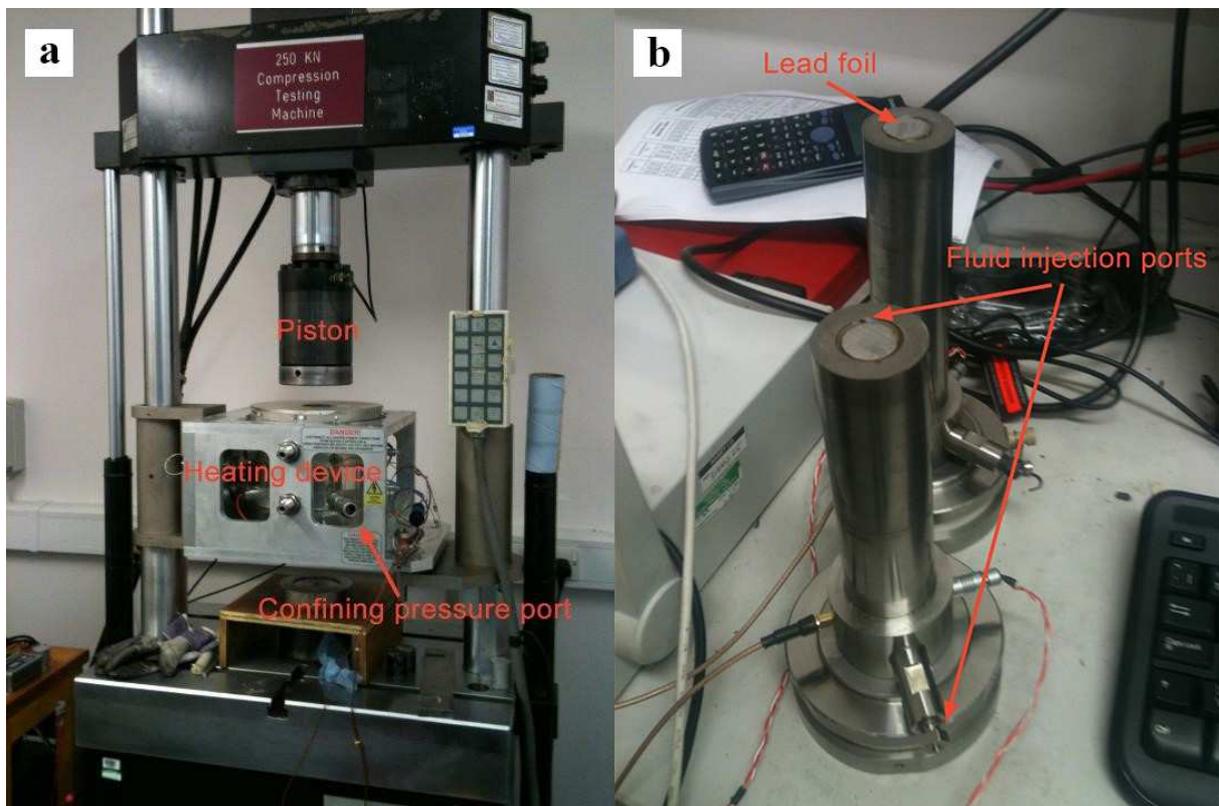
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464 Figures.

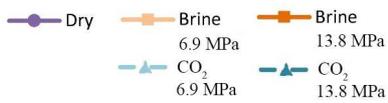
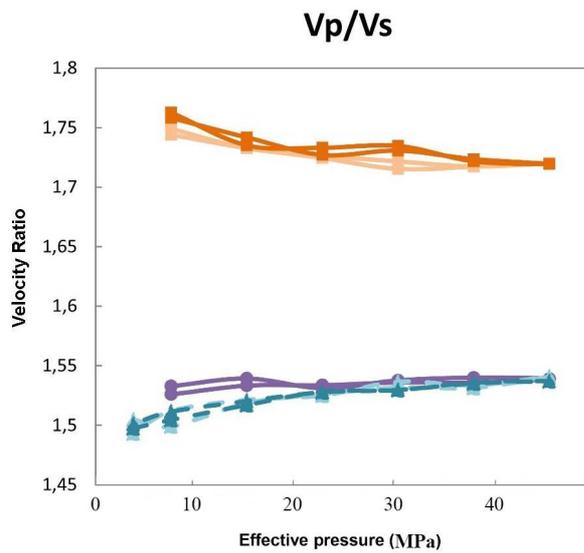
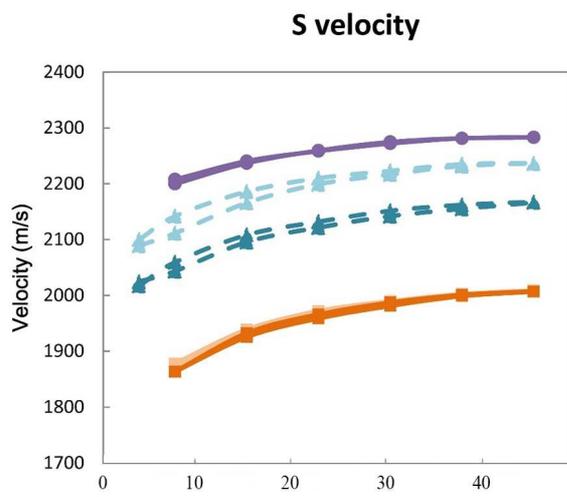
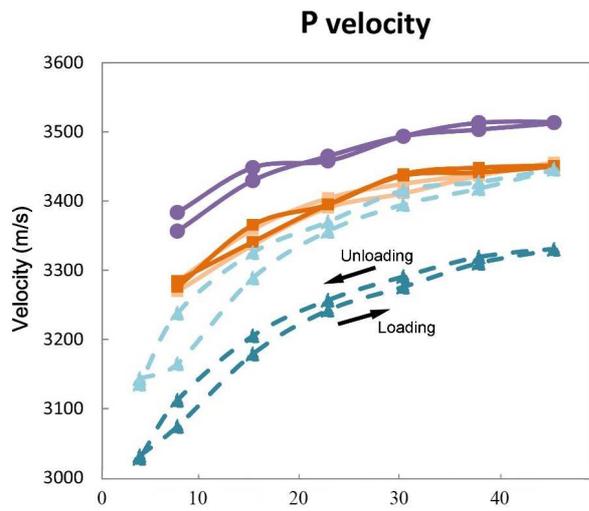


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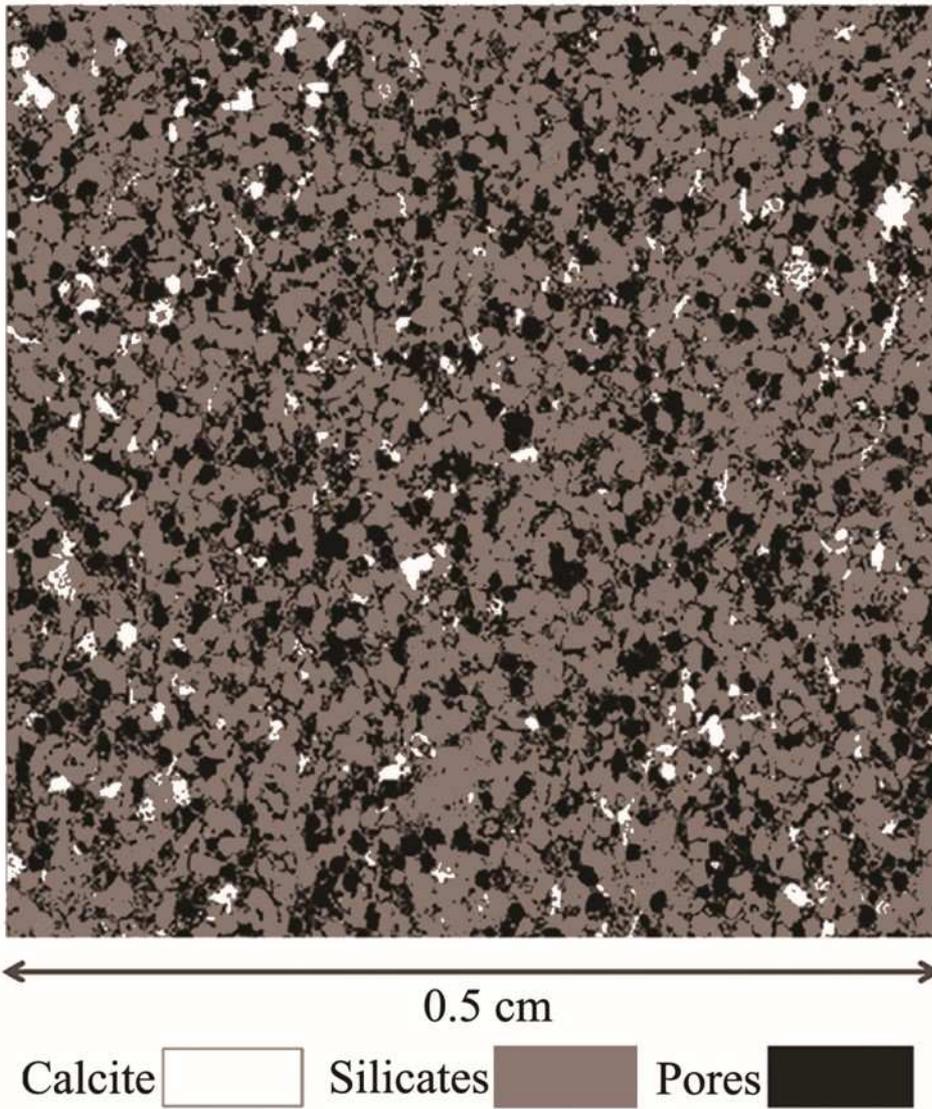
466 Figure 1. a) Triaxial cell equipped with sample heater used for sonic velocity determination. b)

467 Steel platens placed on both sides of the core inside the heater used to generate sonic

468 waves and to inject fluids.

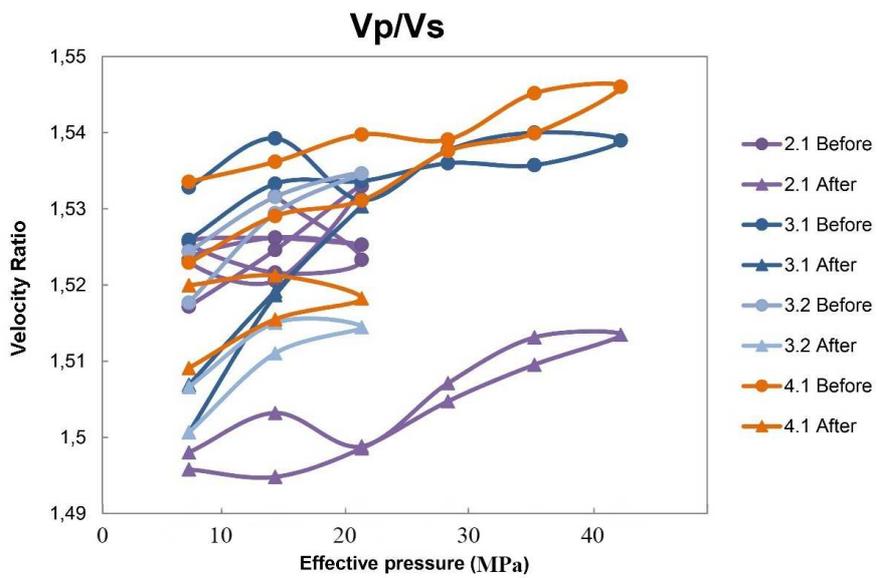
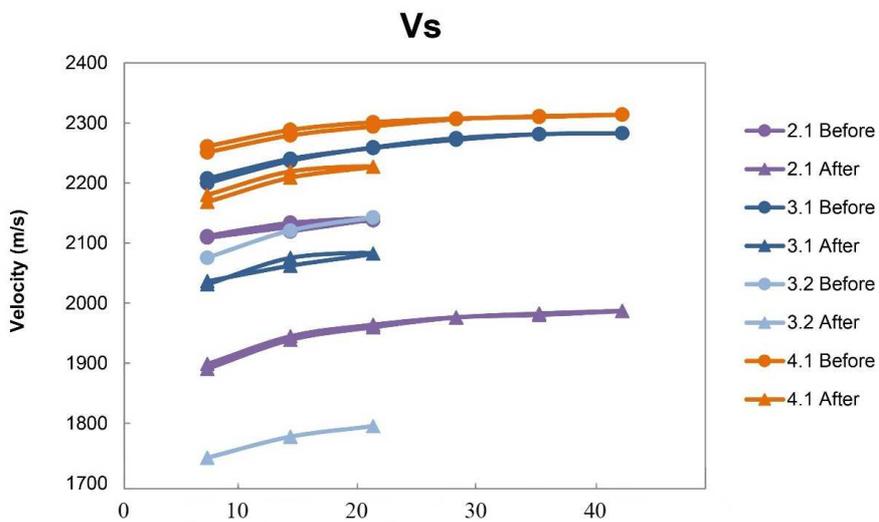
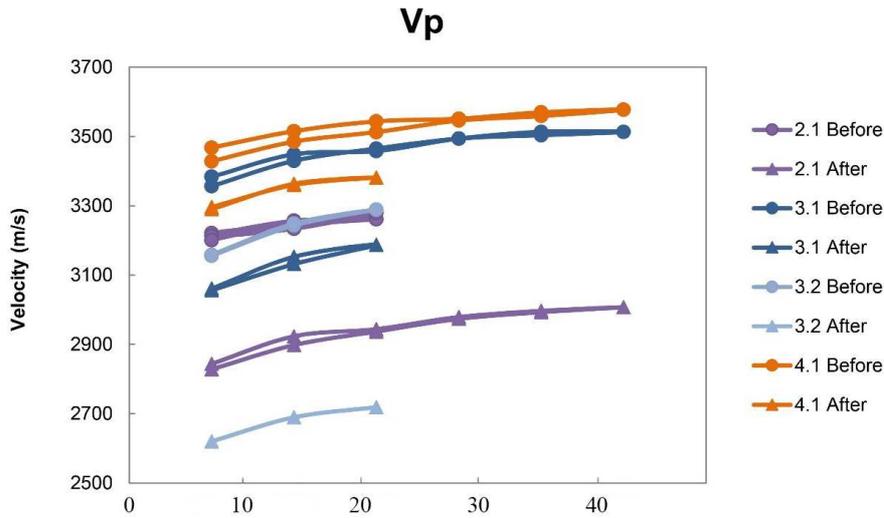


470 Figure 2. Effect of fluid composition and fluid pressure (either 6.9 or 13.8 MPa) on V_p , V_s
471 and V_p/V_s ratio of core 3.1.



472

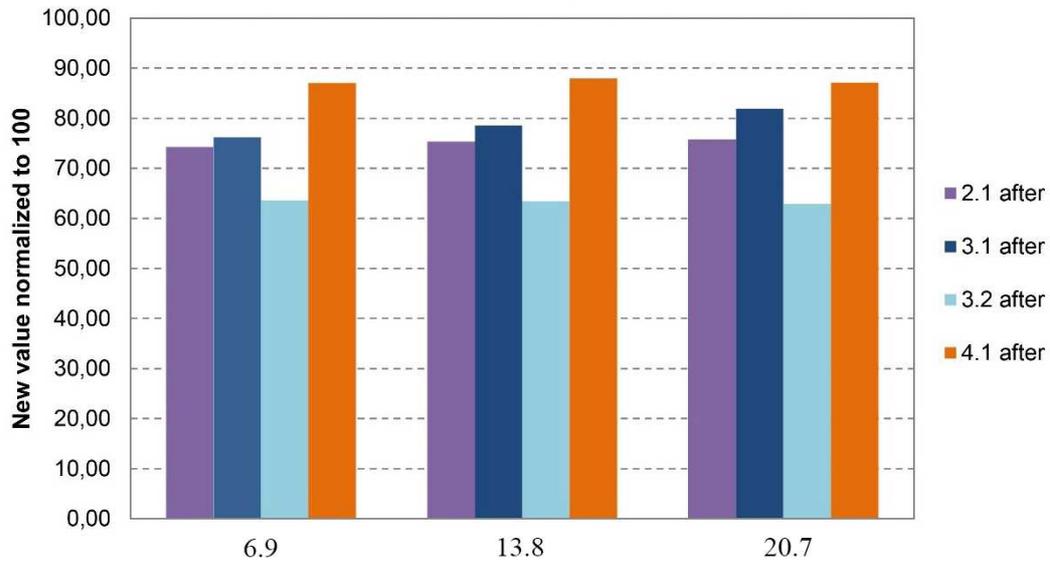
473 Figure 3. Thin section image showing calcite and pores distribution in Cayton Bay sandstone.



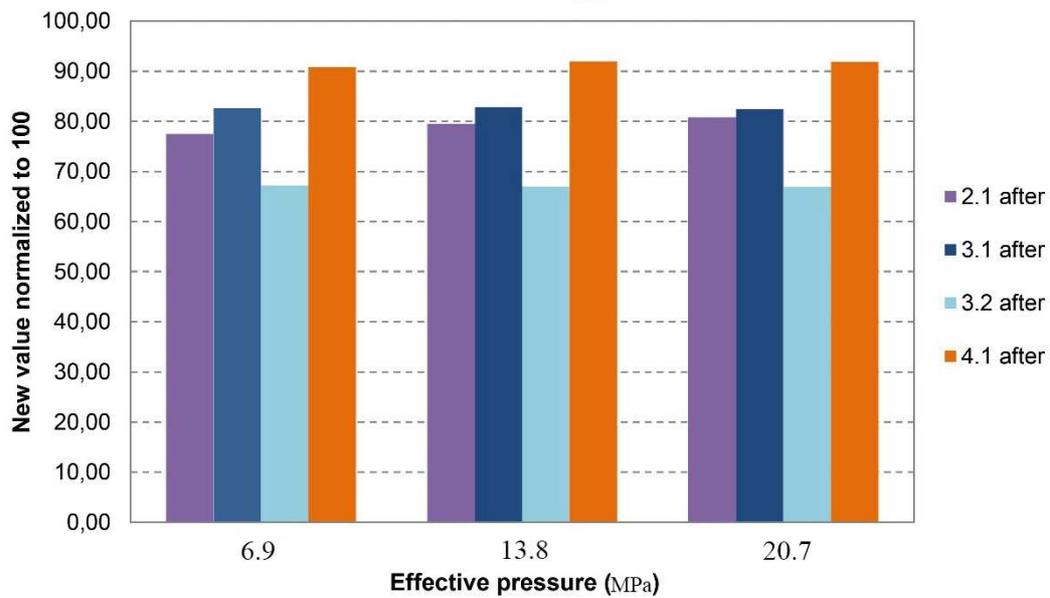
474

475 Figure 4. Comparison of V_p , V_s and V_p/V_s ratio before and after calcite dissolution for four
 476 cores.

Dry bulk modulus relative to initial value at any given P_{eff}



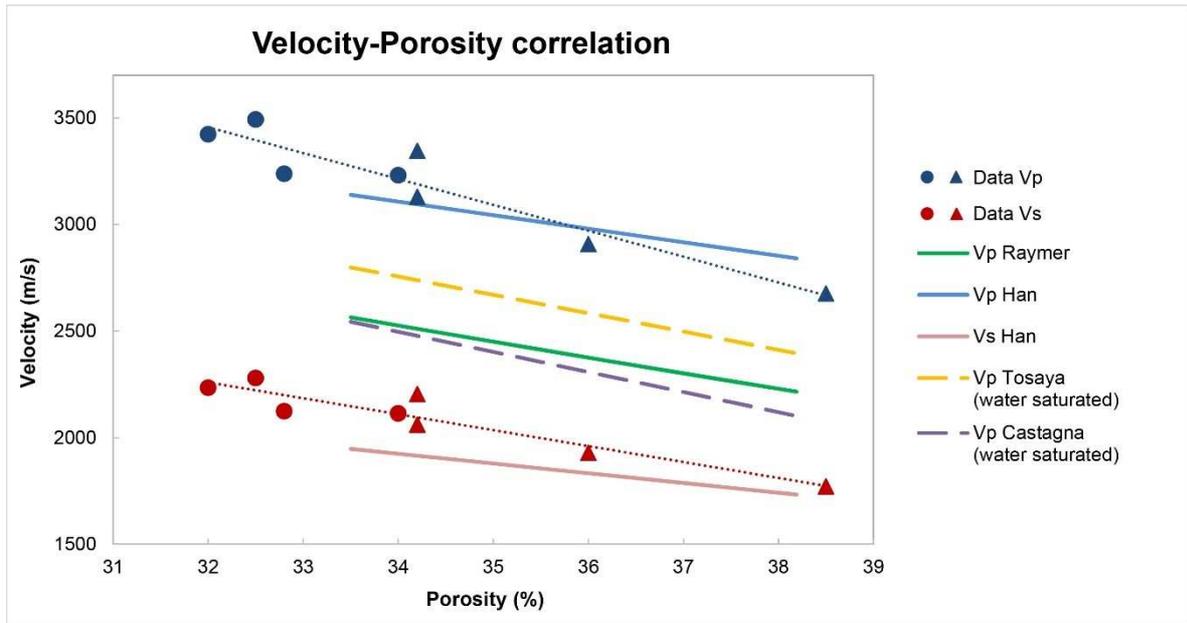
Dry shear modulus relative to initial value at any given P_{eff}



477

478 Figure 5. Change in bulk and shear moduli caused by calcite dissolution at constant effective

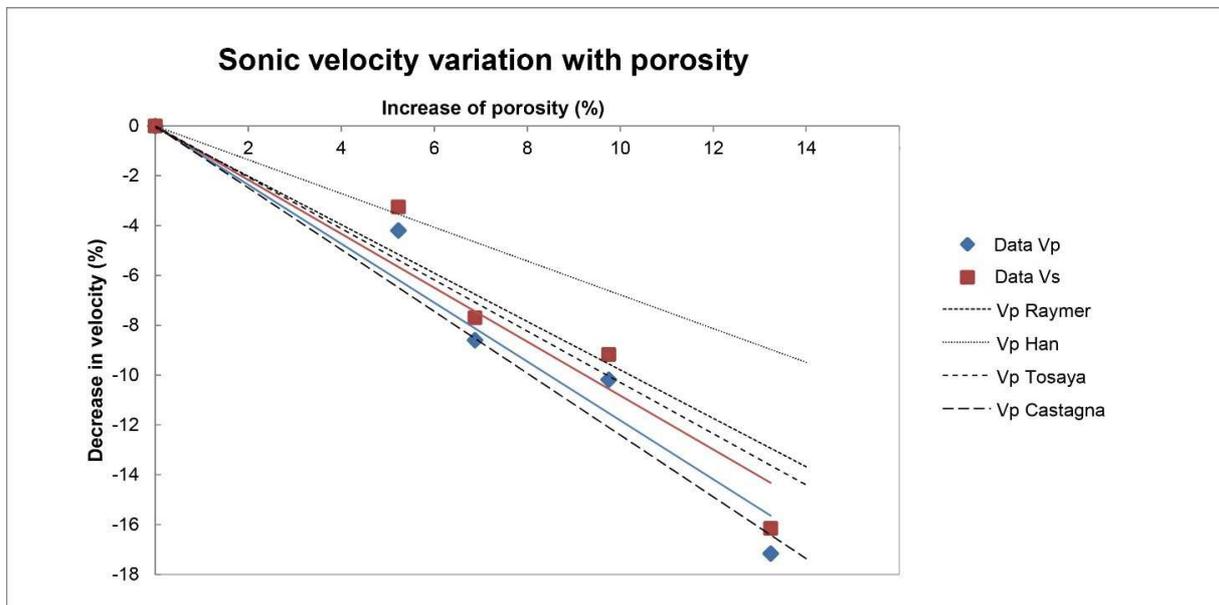
479 pressure.



480

481 Figure 6. Comparison between empirical velocity-porosity correlations and experimental data.

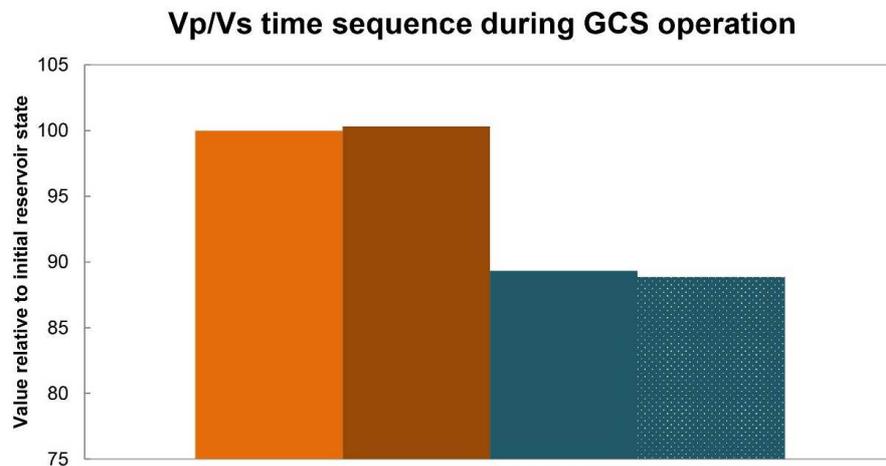
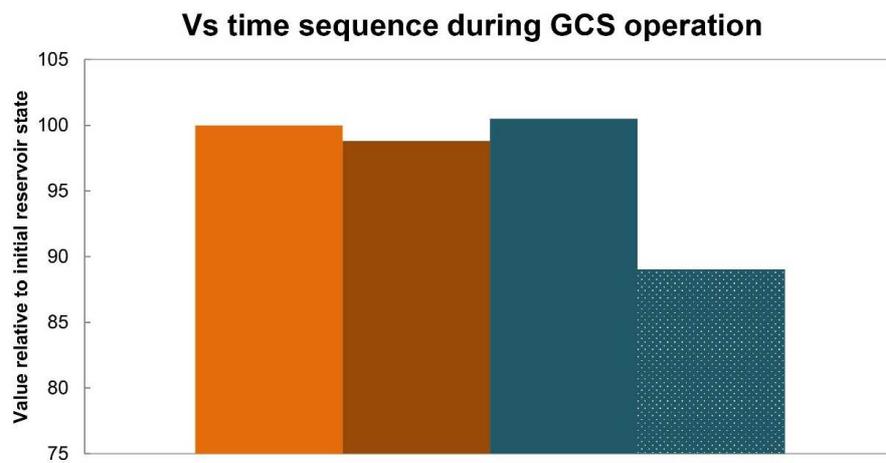
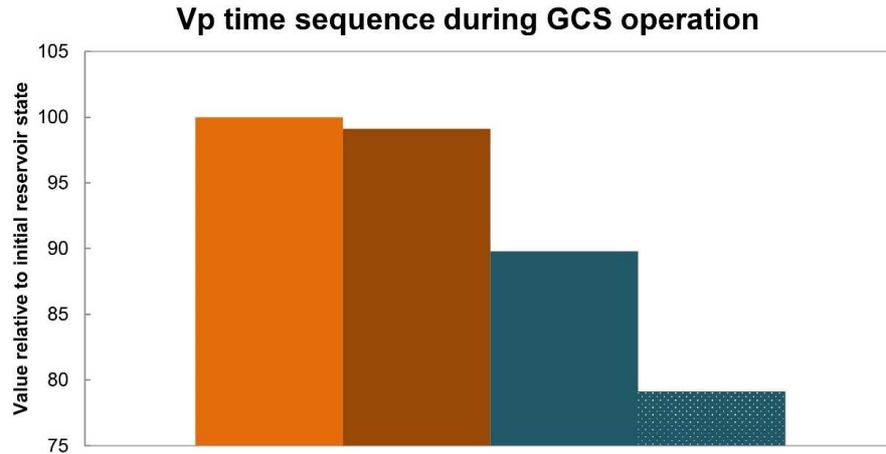
482 Unreacted core data is represented with circles and reacted core data is represented with
 483 triangles.



484

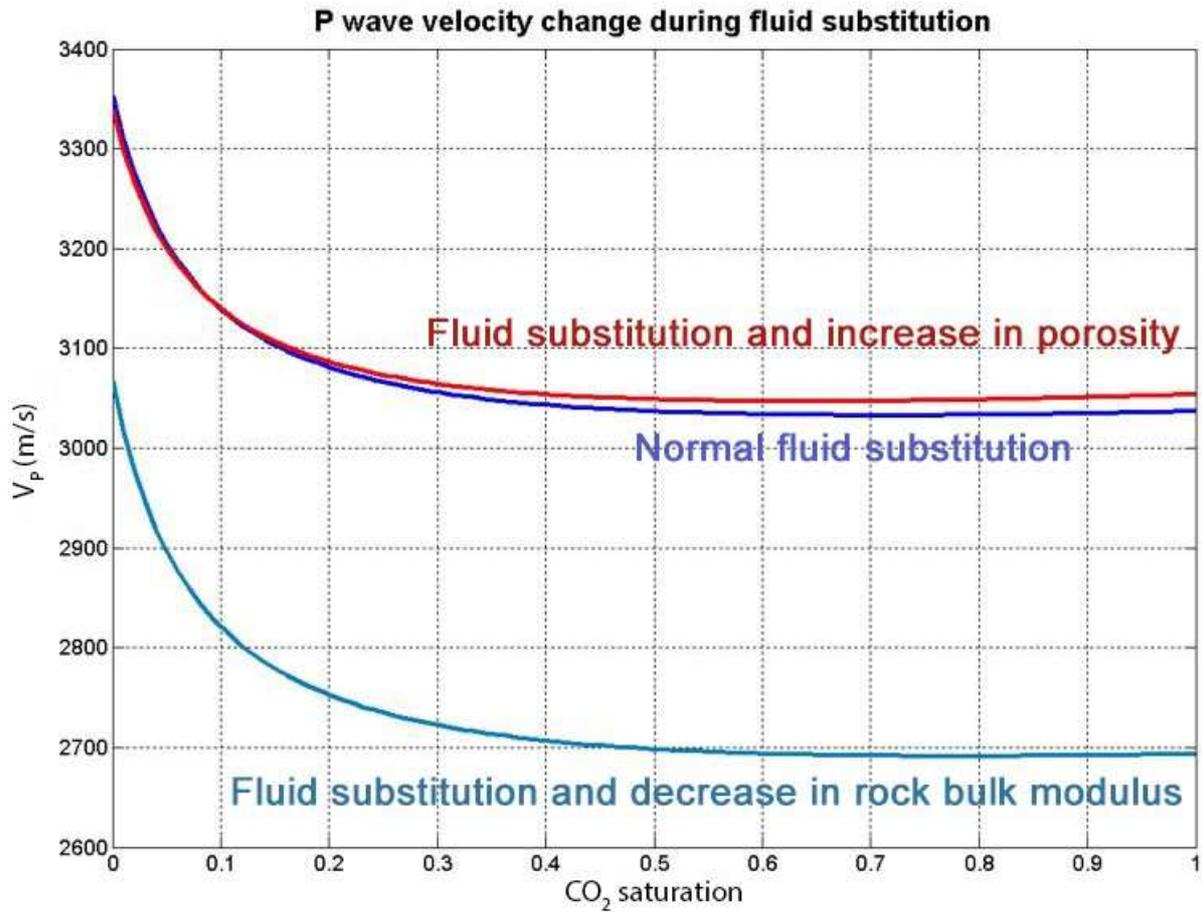
485 Figure 7. Comparison between empirical and experimental variation in velocity with porosity.

486 Linear fit of the experimental data is also shown.



487

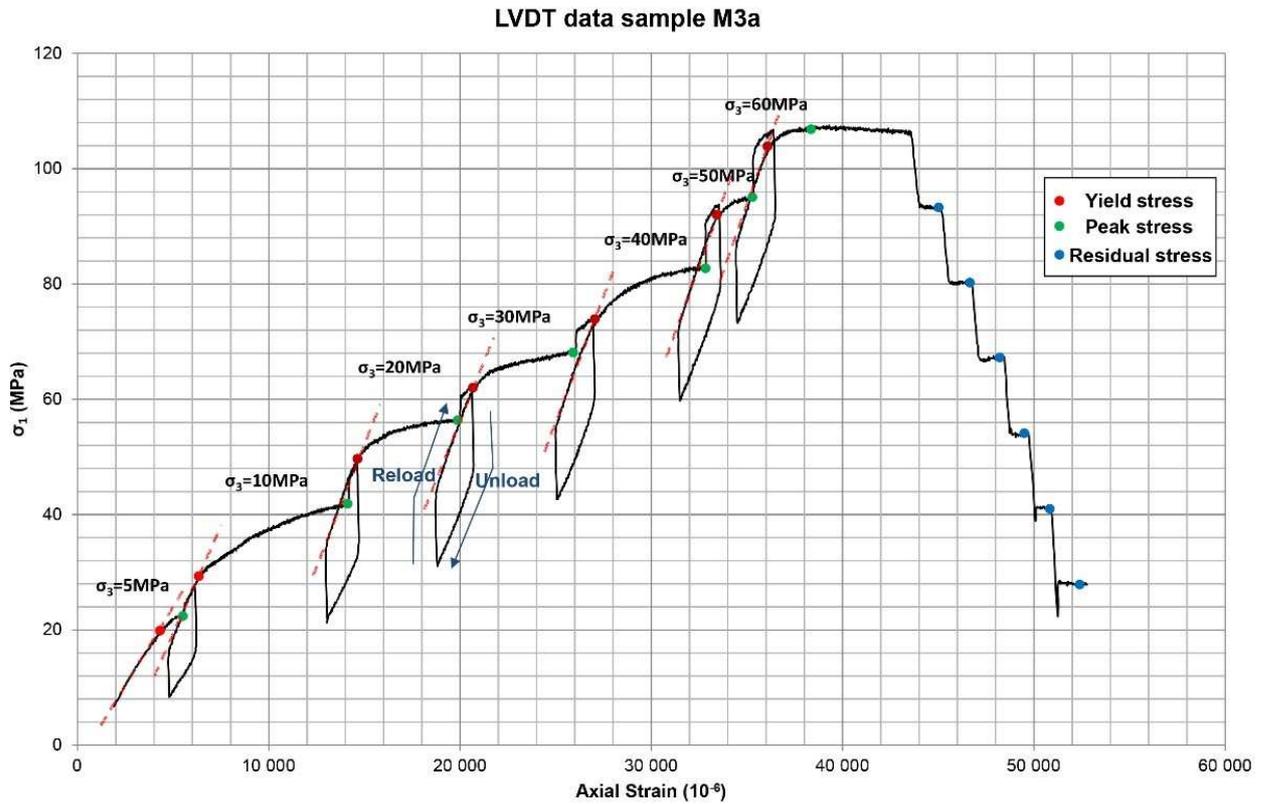
488 Figure 8. Normalized V_P , V_S and V_P/V_S evolution after brine pressurization, CO_2 invasion and
 489 CO_2 invasion plus calcite dissolution. Orange colour stands for brine saturated and blue
 490 for CO_2 -saturated rock. Darker colours means higher fluid pressure. Calcite dissolution is
 491 represented as white dots



492

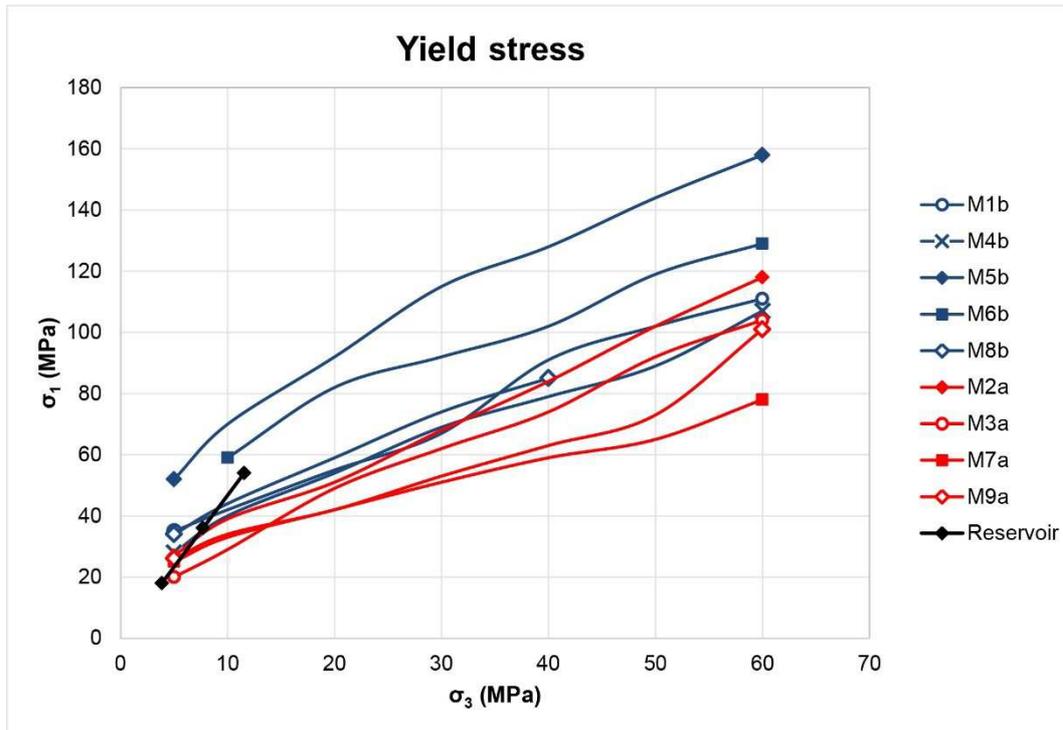
493 Figure 9. Fluid substitution effects on V_p according to Gassmann theory including the effect

494 of a porosity change and the effect of a K_{dry} change.



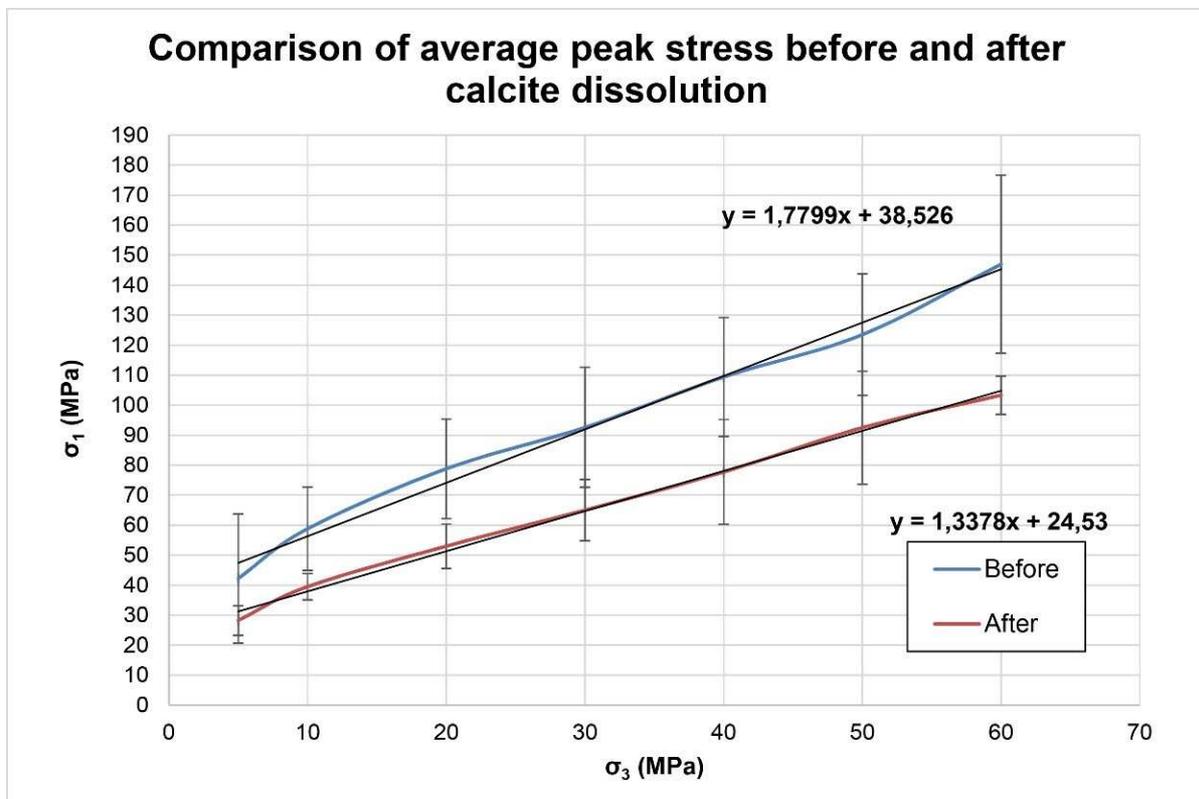
495

496 Figure 10. Example of multiple failure test data. The values of interest have been highlighted
 497 with dotted red guidelines to illustrate the yield stress determination. The unloading and
 498 unloading and reloading paths at the start of new confining pressure stage is also illustrated.



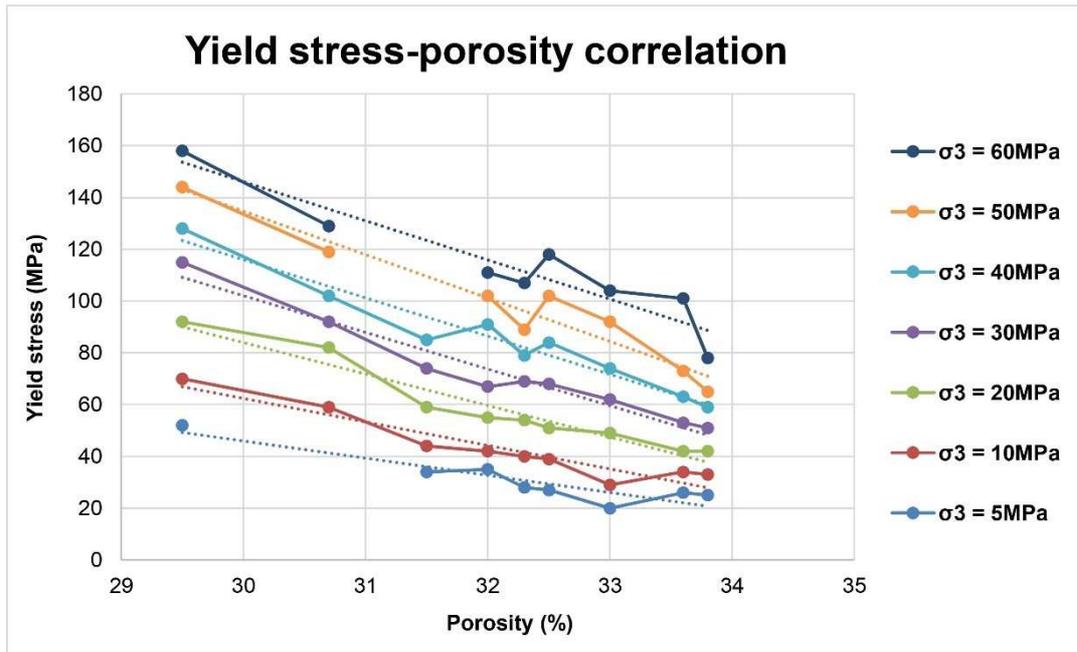
499

500 Figure 11. Yield stress envelopes for all cores and possible reservoir stress state at increasing
 501 depths of 1000, 2000 and 3000 m.



502

503 Figure 12. Linear fit of the average peak stress envelopes before and after dissolution (The
 504 bars represents two standard deviations from the mean). The effect of calcite dissolution
 505 on the rock cohesion (τ_0) is obvious (downward translation of the curve) while its effect
 506 on the angle of internal friction is more ambiguous (change in slope).



507
 508 Figure 13. Experimental data showing the yield stress-porosity correlation. The results
 509 obtained on samples after calcite dissolution are represented as triangles and the results
 510 from unaltered samples are represented as discs. Every data points for a given porosity
 511 represent one single experiment. From left to right is presented the data from samples
 512 M5b, M6b, M8b, M1b, M4b, M2a, M3a, M9a and M7a (where “a” and “b” signifies
 513 “after” and “before” calcite dissolution).

514
 515 Tables.

516 Table 1. Summary of sonic velocity experiments. All cores were drilled from the same sample
 517 block. Some cores were obtained by cutting a longer initial core in two (in that case they were

518 numbered N.1 and N.2). Some cores were used for multiple experiments at various fluid
 519 saturation and fluid pressure conditions.

Core number	Porosity before calcite dissolution	Porosity after calcite dissolution	Saturation conditions	Experiments before and after calcite dissolution	Pore pressure range (psi)
2.1	32.8	36	Dry at T=20°C and 50°C	yes	N/A
3.1	32.5	34.2	Dry/CO ₂ /Brine at T=50°C	yes	500-2000
3.2	34	38.5	Dry at T=50°C	yes	N/A
4.1	32.5	34.2	Dry/CO ₂ at T=50°C	yes	2000-4000
4.2	35.5	N/A	Dry at T=20°C and 50°C	no	N/A

520

521 Table B1. Mineral bulk moduli and volume fraction used for the calculation of the K_m
 522 parameter.

Mineral Name	Volume fraction%	Bulk Modulus (GPa)
Quartz	76	37
Microcline	6	37
Mica	6	50
Calcite	5	77
Smectite	4	20
Kaolinite	1	1.5
Dolomite	1	95

Albite	1	76
Voigt Average		30
Reuss Average		39
VRH Average		34.5

523

524 Table B2. Fluid properties used for the Gassmann modelling

Fluid saturation	Pore pressure (psi)	Fluid density (kg/m ³)	System density	Fluid bulk modulus (GPa)
CO ₂	1000	168	1835	0.009
CO ₂	2000	666	1996	0.073
CO ₂	3000	793	2038	0.176
Brine	1000	1026	2113	2.65
Brine	2000	1026	2113	2.69
Brine	3000	1026	2113	2.72

525