

1 Gassmann fluid substitution and shear modulus variability in carbonates
2 at laboratory seismic and ultrasonic frequencies

3 Ludmila Adam¹, Michael Batzle¹, and Ivar Brevik²

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ABSTRACT

6 Carbonates have become important targets for rock property
7 research in recent years because they represent many of
8 the major oil and gas reservoirs in the world. Some are under-
9 going enhanced oil recovery. Most laboratory studies to un-
10 derstand fluid and pressure effects on reservoir rocks have
11 been performed on sandstones, but applying relations devel-
12 oped for sandstones to carbonates is problematic, at best. We
13 measured in the laboratory nine carbonate samples from the
14 same reservoir at seismic (3 to 3000 Hz) and ultrasonic
15 (0.8 MHz) frequencies. Samples were measured dry (humid-
16 ified), and saturated with liquid butane and brine. Our car-
17 bonate samples showed typical changes in moduli as a func-
18 tion of porosity and fluid saturation. However, we explored
19 the applicability of Gassmann's theory on limestone and dol-
20 omite rocks in the context of shear and bulk modulus disper-
21 sion, and Gassmann's theory assumptions. For our carbonate
22 set, at high differential pressures and seismic frequencies, the
23 bulk modulus of rocks with high aspect ratio pores and dol-
24omite mineralogy is predicted by Gassmann's relation. We
25 also explored in detail some of the assumptions of Gas-
26smann's relation, especially rock-frame sensitivity to fluid
27 saturation. Our carbonate samples showed rock shear-modu-
28lus change from dry to brine saturation conditions, and we in-
29vestigated several rock-fluid mechanisms responsible for this
30change. To our knowledge, these are the first controlled labo-
31ratory experiments on carbonates in the seismic frequency
32range.

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34 INTRODUCTION

35 An important area of research for carbonate rocks is the fluid sub-
36stitution effect on elastic moduli and velocities. One of the widely

used relations to estimate the effect of fluids on bulk modulus is **37**
Gassmann's fluid substitution theory (Gassmann, 1951), which we **38**
will examine in the following section. Laboratory measurements on **39**
carbonates have been performed at ultrasonic frequencies (~0.8 **40**
MHz) to estimate the validity of Gassmann's equations for lime- **41**
stones and dolomites (Wang et al., 1991; Marion and Jizba, 1997; **42**
Wang, 2000; Baechle et al., 2005; Røgen et al., 2005). In most **43**
cases Gassmann's predictions underestimate the observed ultra- **44**
sonic velocities for either oil- or brine-saturated samples, al- **45**
though for some samples Gassmann theory overestimates the **46**
measured velocities (Wang, 2000; Baechle et al., 2005; Røgen et **47**
al., 2005). **48**

Presently, the applicability of Gassmann's equation to carbonate **49**
rocks is unresolved. With our work, we hope to make inferences **50**
about the uncertainties and interpretation on the applicability of **51**
Gassmann's equation. Our work focuses on understanding the appli- **52**
cability of Gassmann's fluid substitution theory at seismic and ultra- **53**
sonic frequencies. We also analyze the validity of some of the as- **54**
sumptions for Gassmann's theory, especially rock-frame sensitivity **55**
to fluids. Our carbonate samples consist of different fabrics, mineral- **56**
ogies, porosities, and permeabilities; still we must be careful in gen- **57**
eralizing our results to all carbonate reservoirs. **58**

First, we present Gassmann's theory and its assumptions. Second, **59**
we describe the laboratory acquisition, processing, and data uncer- **60**
tainty analysis at seismic and ultrasonic frequencies. Then, we intro- **61**
duce shear modulus variability with fluid substitution and the possi- **62**
ble mechanisms that could explain these changes. Finally we com- **63**
pare our measured bulk modulus to Gassmann's predictions for **64**
these carbonate rocks. **65**

GASSMANN'S EQUATION 66

Gassmann's fluid substitution relation is commonly applied to **67**
predict the bulk modulus for rocks saturated with different fluids: **68**

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¹Colorado School of Mines, Center for Rock Abuse, Department of Geophysics, 1500 Illinois Street, Golden, Colorado 80401. E-mail: ladam@mines.edu; mbatzle@mines.edu.
²Statoil Research Centre, Posttuttak, N7500 Trondheim, Norway. E-mail: ivb@statoil.com.
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$$K_{sat} = K_{dry} + \frac{\left(1 - \frac{K_{dry}}{K_{min}}\right)^2}{\frac{\phi}{K_{fl}} + \frac{1 - \phi}{K_{min}} - \frac{K_{dry}}{K_{min}^2}} \quad (1)$$

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70 Gassmann's equation 1 estimates the saturated bulk modulus (K_{sat})
 71 through the bulk modulus of the forming minerals (K_{min}), the bulk
 72 modulus of the frame or dry rock (K_{dry}), the bulk modulus of the fluid
 73 (K_{fl}), and the rock porosity (ϕ) (Gassmann, 1951). Note that in Gas-
 74 smann's relation, the considered property of the fluid in the rock is
 75 only the fluid bulk modulus.

76 Gassmann's derivation is based on the following assumptions for
 77 a porous system: (1) Pore pressure is in equilibrium between pores.
 78 This can be achieved at very low frequencies, usually at seismic fre-
 79 quencies or lower, where the fluid has enough time to reach relax-
 80 ation or equilibrium. However, the relaxation time depends also on
 81 fluid viscosity and density, and rock permeability. (2) The porous
 82 frame consists of a single solid material (monomineralic). (3) Pores
 83 are in flow communication and are homogeneously, fully filled with
 84 a nonviscous fluid. (4) The system is closed (undrained). (5) The
 85 pore fluid does not chemically influence the solid frame. Although
 86 implied, a constant rock shear modulus from dry to any fluid-type
 87 saturation is not an assumption but an outcome of Gassmann's theo-
 88 ry (Berryman, 1999).

89 The beauty of equation 1 is its simplicity as well as the fact that the
 90 variables have physical significance and are usually well con-
 91 strained or can be directly measured. Other fluid substitution theo-
 92 ries require the knowledge of such factors as the symmetry of the
 93 rock, the geometry of the inclusions, and the crack density among
 94 others. For example, in the low-frequency limit, where no pore-pres-
 95 sure gradients exist, Brown and Korringa (1975) relate the aniso-
 96 tropic rock effective elastic compliance tensor to the same rock filled
 97 with fluid, and for an isotropic and monomineralic rock, their rela-
 98 tions reduce to Gassmann's equation. For this fluid-substitution theo-
 99 ry, knowledge of the anisotropic symmetry and pore-space compres-
 100 sibility are required. Other fluid substitution theories mostly
 101 assume isolated inclusions and their geometries in the derivation of
 102 the equations. Isolated cavities should then also be isolated with re-
 103 spect to fluid flow (presence of pore-pressure gradients). Therefore,
 104 theories that assume isolated inclusions (Kuster and Toksoz, 1974;

O'Connell and Budiansky, 1974; Hudson, 1981) may be more appli-
 cable to the high-frequency range and require knowledge of param-
 eters related to pore space.

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CARBONATE SAMPLES

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Our carbonates are from two wells in a single reservoir with
 depths between 2915 and 3180 m below sea level. The reservoir has
 lagoon, ramp and shoal depositional environments. These different
 depositional systems create different textures, porosities and perme-
 abilities (Figure 1). Some reservoir regions have been dolomitized.
 Dolomitization is evident from high porosity and high permeability
 because dissolved grains or fossils become pore space, increasing
 the connectivity between pores, thus increasing permeability. The
 reservoir is not fractured and has few clay minerals, but does have
 minor anhydrite. The available samples comprise nine carbonates
 with varying porosity (5%–35%), permeability (0.001–800 mD),
 mineralogy (dolomite and limestone), and texture. The samples are
 either almost pure calcite or dolomite (95% total volume) with less
 than 3% clays and 5% anhydrite of total volume. Samples with large
 anisotropy or vuggy pores are avoided. Table 1 summarizes the pet-
 rological data for our samples. Porosity and permeability are mea-
 sured using standard helium porosimetry and air permeability equip-
 ment at atmospheric pressure. Permeability values are corrected for
 Klinkenberg gas slippage. The samples are cylindrical, 3.75 cm in
 diameter and 3.75 to 5 cm in length.

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Velocity and elastic modulus data are acquired at nine pressure
 points. Confining pressure varies from 3.5 to 34.5 MPa while pore
 pressure is held constant at 3.5 MPa, thus reaching a maximum dif-
 ferential pressure of 31 MPa. The low-frequency system in the labo-
 ratory is pressurized with nitrogen gas, but for safety reasons the sys-
 tem is not able to reach the reservoir differential pressure
 (34.5 MPa). Samples are measured dry, under butane (C_4H_{10}), and
 brine (200,000 ppm NaCl) saturations. Butane, at 3.5 MPa, is in
 liquid state. Samples are measured with some amount of moisture
 because even less than 1% of water can reduce the bulk and shear
 moduli significantly (Clark et al., 1984). Because samples show sen-
 sitivity to water, several are kept in a high-humidity chamber to pro-
 vide an initial brine saturation (less than 1%). Samples A, C, E, F and
 G are humidified previous to measurements, thus *dry* for these sam-
 ples means humidified. Samples B, D, H and I are measured at room
 conditions (30% humidity). Samples are coated with a thin, imper-
 meable polyimide film (Kapton), over which strain gauges are glued
 to measure rock deformations at seismic frequencies. This film
 keeps the moisture inside the rock and prevents nitrogen diffusion.

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DATA EXAMPLE: ACQUISITION AND PROCESSING

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Samples are measured at low (seismic: 3–3000 Hz) and ultrason-
 ic frequencies (~0.8 MHz), although sample G is measured at ul-
 trasonic frequencies only. Seismic frequency moduli and velocities
 are derived from the strain-stress method (Spencer, 1981; Batzle et
 al., 2006). Measured strains on the rock and a calibrating material
 (aluminum) are converted into Young's modulus and Poisson's ratio,
 and from these we get bulk and shear moduli. Batzle et al. (2006)
 give a detailed description of the apparatus and the estimation of
 elastic moduli from measured strains. In the stress-strain experi-
 ment, we directly estimate the bulk and shear moduli. Thus, our
 moduli estimates are independent of the rock density. As we will see,

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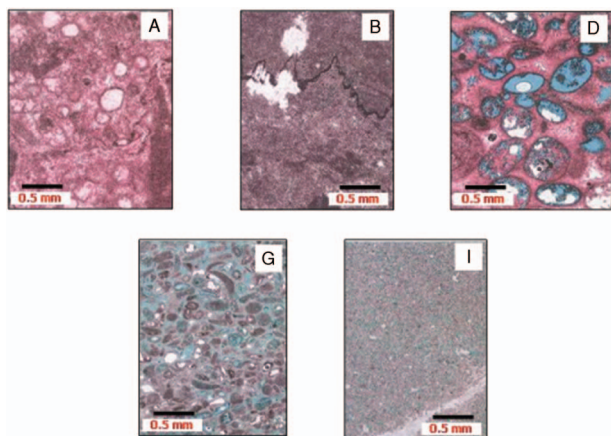


Figure 1. Thin sections for some of our carbonate samples. Pink represents calcite, gray dolomite, white anhydrite and blue pore space.

161 for ultrasonic data the rock density *is* needed to estimate the bulk and
162 shear moduli.

163 For ultrasonic data, we measure the time a wave takes to propa-
164 gate from the top of the sample to the bottom (Birch, 1960). The ve-
165 locity, either P- or S-wave, is estimated by: $V = (L - \delta L)/(T_m - T_0)$,
166 where L is the sample length measured at atmospheric pressure, δL is
167 the change in sample length due to pressurization, T_m is the measured
168 travel time, and T_0 is a time correction. δL is ignored because the
169 change in length, which we can estimate from the low-frequency ex-
170 periment, is very small. T_0 , the travel time through the aluminum
171 material between the ultrasonic transducer and the sample, is known
172 and constant for all measured samples. Therefore, we can rewrite the
173 velocity as simply: $V = L/T$, where T is the corrected travel time. As-
174 suming isotropy, the measured velocities and densities are then used
175 to derive the shear and bulk moduli.

176 As an example of the estimated bulk modulus over the entire fre-
177 quency range, we show results for sample *H* in Figure 2. The compu-
178 tation of the error bars and the linear fit are discussed later in this sec-
179 tion. Observe that the rock bulk modulus increases with saturating
180 fluid. However, the change in rock bulk modulus from dry to butane
181 saturated is small compared to when the rock is saturated with brine.
182 This is because butane has a lower fluid bulk modulus than brine.
183 Figure 2 also shows bulk modulus dispersion (higher frequencies
184 have a larger modulus). Several theories exist to explain the nature of
185 this dispersion. A primary cause for dispersion can be pore-pressure
186 disequilibrium caused by nonzero pore-pressure gradients. This un-
187 relaxed pressure is described by several mechanisms: grain-fluid in-
188 erial and viscous coupling (Biot, 1956), patchy saturation (White,
189 1975; Dutta and Ode, 1979) and squirt or local fluid flow (Mavko
190 and Jizba, 1991), among others. Our goal here is not to decide which
191 of frequency dependent modulus or velocity theories are causing the
192 dispersion. We do want to point out differences in modulus estimates
193 as a result of the dispersion from seismic to ultrasonic frequencies.
194 As previously mentioned, Gassmann's theory is the low-frequency
195 limit, meaning that this theory may not be suitable to predict ultra-
196 sonic data because of possible dispersion in the elastic moduli and
197 velocities. Wang (1997), Marion and Jizba (1997), Baechle et al.
198 (2005) and Røgen et al., 2005 have shown how, in most cases, Gas-
199 smann's theory underpredicts ultrasonic frequency measurements.

200 Pore pressure can equilibrate if there is enough time for the fluids to
201 relax. This means there is a characteristic frequency, f_c of the rock
202 perturbation. For measurements acquired at a frequency less than f_c ,
203 the pore pressure has reached equilibrium, while for higher frequen-
204 cies than the f_c , pore fluids are not equilibrated, producing higher
205 values for modulus and velocity.

206 Differential pressure also controls the modulus dispersion of a
207 rock. At low-differential pressures where compliant pores or cracks
208 are open, pore-pressure disequilibrium is more likely to occur. Wang
209 (2000) shows, in a compilation of ultrasonic laboratory data of car-
210 bonate samples, that Gassmann's theory substantially (up to 30%)
211 underpredicts the measured velocities at low-differential pressures.
212 At high-differential pressures, compliant pores close, and Gas-
213 smann's theory predicts the measured data within 10%.

214 Carbonates are heterogeneous and vugs or moldic structures can
215 have comparable length to the ultrasonic wavelength (0.5 cm for a
216 wave at 0.8 MHz and with a velocity of 4500 m/s). Some of our
217 samples showed inclusions of different densities or voids with di-
218 mensions on the order of ultrasonic wavelengths. Therefore, scatter-
219 ing of ultrasonic waves is possible in carbonate samples, especially
220 in dry rocks where the density contrast between voids and the matrix
221 is large. When scattered, the wave loses energy to multiple reflec-
222 tions from grains, mostly resulting in lower moduli and velocities at
223 higher frequencies. The larger modulus contrast will be for air-grain
224 and butane-grain interfaces.

Poisson's ratio: a correction

225 Samples *B*, *F* and *I* show higher values of Poisson's ratio at low
226 frequency than expected in carbonates. Rock heterogeneity is proba-
227 bly not the cause, since placing the strain gauges on large heteroge-
228 neities (visible to the eye) on measured core plugs are avoided. The
229 observed larger deformations of the sample in the horizontal direc-
230 tion probably result from end effects in our stress-strain system. This
231 large deformation or bulging can result from the combination of in-
232 trinsically large Poisson's ratios in carbonates (>0.25) and short
233 samples (our sample length is close to its diameter). This bulging has
234 been confirmed with preliminary finite-element modeling at our lab-
235 oratory. Poisson's ratio depends on the V_p/V_s , but because the dis-
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Table 1. Petrological data for the carbonate set. Mineralogy was obtained from XRD analysis and are reported in percent per volume (samples E, G and H had no XRD analysis). Mineral bulk modulus is computed using Voigt-Reuss-Hill average. Texture follows modified Dunham's carbonate classification (Moore, 2001): mud=mudstone, wacke=wackestone, pack=packstone, grain=grainstone, and bound=boundstone.

SAMPLES	A	B	C	D	E	F	G	H	I
Porosity	1.6	4.6	21.0	24.9	28.5	34	23.6	29.6	34.7
Permeability (mD)	0.03	0.03	5.50	1.20	0.43	0.31	25.00	103.00	432.00
Grain density (gm/cm ³)	2.73	2.84	2.70	2.71	2.70	2.69	2.84	2.80	2.86
Calcite (%)	83.0	0.7	76.0	99.6	–	97.0	–	–	0.4
Dolomite (%)	11.0	97.0	21.0	0.0	–	0.0	–	–	93.0
Anhydrite (%)	0.5	0.5	0.0	0.0	–	0.7	–	–	4.9
Phyllosilicates (%)	3.4	0.8	2.4	0.0	–	2.3	–	–	1.1
Quartz (%)	0.6	0.6	1.2	0.4	–	0.2	–	–	0.8
K-feldspar (%)	2.0	0.0	0.0	0.0	–	0.0	–	–	0.0
Mineral bulk modulus (GPa)	70.70	78.96	71.59	71.26	71.59	70.35	85.00	78.96	77.67
Texture	Wacke	Mud	Grain	Grain	Grain	Bound	Pack	Wacke	Mud

237 person in V_p and V_s are similar for our samples, the resulting disper-
 238 sion in Poisson's ratio is negligible, making it possible to correct the
 239 low-frequency data with the estimates we obtain from ultrasonic
 240 data. Domenico (1984), Anselmetti and Eberli (1993), Mavko et al.
 241 (1998), Assefa et al. (2003), and Han (2004, Fluids and DHI Consor-
 242 tia Meeting Report) measured carbonate samples ultrasonically and
 243 derived empirical relations for V_p and V_s . We use their relations to
 244 compute Poisson's ratio for water/brine saturated carbonates and
 245 compare their values to our samples' Poisson's ratios measured at ul-
 246 trasonic frequencies (Figure 3). Agreement between modeled Pois-
 247 son's ratio and our measurements lets us use the ultrasonic values to
 248 correct the Poisson's low-frequency data. The correction consists of
 249 multiplying the seismic frequency Poisson's ratio by a factor less
 250 than one. This factor is obtained from the ratio of the ultrasonic and
 251 the biased seismic frequency Poisson's ratios.

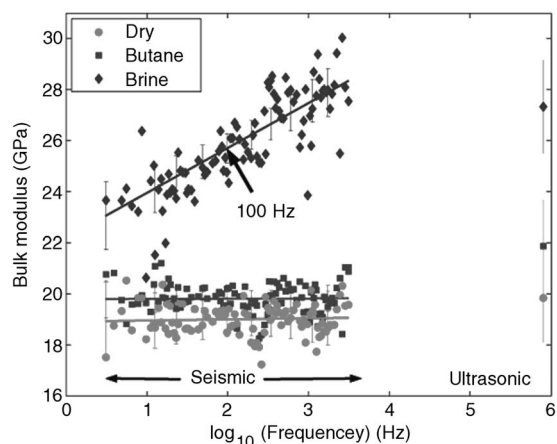


Figure 2. Seismic and ultrasonic frequency bulk modulus least-squares estimates (solid lines) and measured data for sample *H* at 31 MPa. Observe the modulus dispersion for different fluids. Error bars are two standard deviations of the estimated bulk modulus.

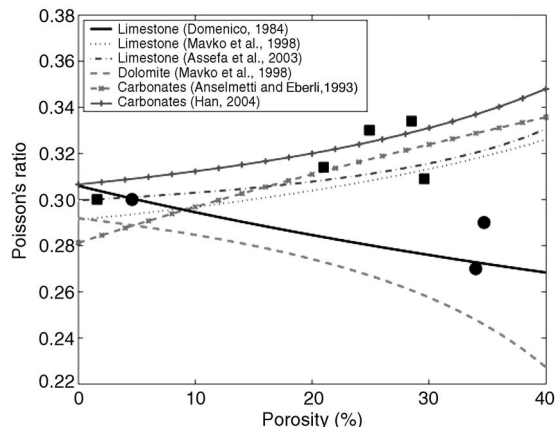


Figure 3. Modeled Poisson's ratio from empirical relations from ultrasonic data for carbonate rocks saturated with water/brine. Squares and circles are the Poisson's ratio obtained from our measurements at ultrasonic frequencies. This plot shows that our values of Poisson's ratio are in agreement with the empirical equations. Therefore, we use the ultrasonic Poisson's value to correct the low-frequency data for three of our samples (*B*, *F* and *I*) represented by circles.

Uncertainty analysis

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Our data set consists of Poisson's ratio and Young's modulus as a function of frequency and differential pressure (seismic frequency), and travel time as a function of differential pressure (ultrasonic frequency). We assume that the Poisson's ratio and Young's modulus relation to the logarithm base 10 of frequency is linear, while the travel time with differential pressure follows a second order polynomial (*true* models). We also assume that the error between our data and these *true* models is random, Gaussianly distributed and with zero mean. Our core analysis is performed under the assumption that all requirements for Gassmann's theory applicability are satisfied. If our samples and experimental setup violate one (or more) of the assumptions of Gassmann's theory, we introduce a bias (systematic error) in our estimates, and we will give an interpretation to why some results on the samples do not obey Gassmann's assumptions.

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Stress-strain methodology

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In Figure 4 we plot data for the stress-strain experiment (E and ν) showing a linear trend with \log_{10} of frequency. We fit a straight line to our data and estimate the variance of our random error. We use the variance of the random error to compute the error of estimates of Young's modulus and Poisson's ratio, and later propagate this error into the estimates of bulk and shear moduli. Young's modulus of aluminum equals 70 GPa (needed to compute the rock Young's modulus), and we assume this value is error-free for the uncertainty analysis. On average, our estimates of the standard deviation of the estimated bulk modulus is 1.2 GPa, and that of the shear modulus is 0.3 GPa for seismic frequencies.

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Ultrasonic pulse propagation

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In addition to low frequency measurements, we have travel times at 0.8 MHz versus differential pressure. Travel time decreases with increasing differential pressure (higher velocity). Figure 5 shows this dependence, resulting from open cracks and compliant pores at low-differential pressures. A second order polynomial is fit to the ultrasonic travel time data as a function of pressure (dashed and solid lines in Figure 5), and we obtain the variance of the random error. We then compute the error of our estimated travel times.

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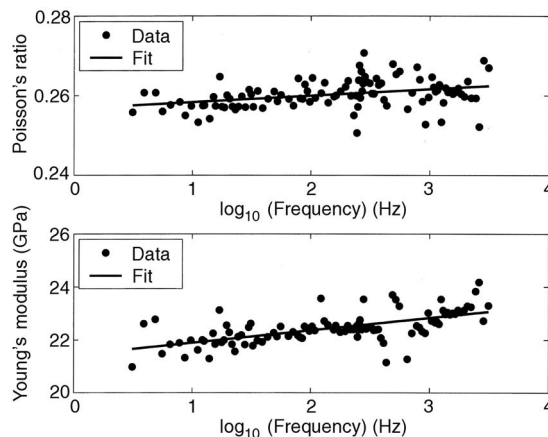


Figure 4. Error analysis on sample *C* at a differential pressure of 17.5 MPa and butane saturation. From the least-squares fit we estimate the variance in our estimate of E and ν .

288 The ends of our samples are machine flattened and when the
 289 length is measured repeatedly, no significant variability is observed,
 290 so we consider that the length is error-free. We also assume there is
 291 no error in the differential pressure measurements. Therefore, we
 292 propagate only the estimated travel-time error into the P- and
 293 S-wave velocity. Now, to estimate the bulk and shear moduli, we
 294 need the rock density which depends on porosity, grain density, and
 295 fluid density. We will assume that the variance of the rock density is
 296 0.5% (which is in the lower end of errors reported in core measure-
 297 ments). In this way we propagate the error in S-wave velocity and
 298 rock density into the shear modulus; then we propagate the P-wave
 299 velocity, rock density and shear-modulus variance into the bulk
 300 modulus. On average, one standard deviation of the estimated P- and
 301 S-wave travel times is small ($\hat{\sigma}_t = 0.06 \text{ } \eta\text{s}$). Still, a small error in the
 302 rock density (0.5%) significantly affects the error of the bulk and
 303 shear moduli estimates ($\hat{\sigma}_K = 2.4 \text{ GPa}$ and $\hat{\sigma}_\mu = 0.8 \text{ GPa}$) com-
 304 pared to the errors for data from the stress-strain experiment.

305 Frequency averaging

306 Because we acquired data for many frequencies, for the purposes
 307 of comparison we limit our analysis to 100 Hz which is representa-
 308 tive of seismic frequency. This distinct frequency value, together
 309 with the ultrasonic data, gives us estimates of dispersion for the bulk
 310 and shear moduli. To estimate the rock moduli at 100 Hz, we apply a
 311 least-squares fit to the logarithm (base 10) of frequency versus Pois-
 312 son's ratio and Young's modulus for each sample and saturation and
 313 pick data at 100 Hz. Figure 2 is an example relating the estimated
 314 (solid line) and measured (symbols) bulk moduli for sample *H*. This
 315 procedure is only for smoothing purposes. We do not claim that this
 316 linearity fully describes the dispersion relation.

317 VARIATIONS IN SHEAR MODULUS

318 Fluids have a shear modulus of zero, so we expect the dry-or fluid-
 319 saturated rock shear modulus to be constant (true for many rocks that
 320 are isotropic and homogeneous). Together with the assumption in
 321 Gassmann's theory that pore fluids do not chemically alter the me-
 322 chanical properties of a rock, Gassmann's theory predicts that the
 323 shear modulus will remain constant under different saturations.
 324 Thus, a measure of the shear modulus is one way to validate Gas-
 325 smann's theory.

326 However, our carbonate samples show rock shear modulus
 327 changes, from dry to brine saturation, of up to 20%. Several labora-
 328 tory studies have also reported shear modulus changes between 5%
 329 and 20% from dry to water or brine saturation in carbonates (Vo-
 330 Thanh, 1995; Assefa et al., 2003; Baechle et al., 2005; Røgen et al.,
 331 2005; Sharma et al., 2006). The shear modulus of the rock is also sen-
 332 sitive to small amounts of moisture or partial saturation of water
 333 (Clark et al., 1984).

334 Rock weakening resulting from fluids has also been observed in
 335 field data. Water, weakening the rock frame in carbonates, is invoked
 336 as a primary factor controlling subsidence of the Ekofisk field. Sylte
 337 et al. (1999) show that compaction of Ekofisk chalks occurs only in
 338 chalks that are being water flooded. High porosity chalks that have
 339 original water content (prewater flooding) are not compacting and
 340 behave elastically throughout the lifetime of the field. They con-
 341 clude that the injected water weakens invaded chalks resulting in
 342 compaction and porosity loss. In their study, they compare observa-
 343 tion to geomechanical models, but do not give the physical-chemical
 344 mechanisms that could be producing this weakening.

Khazanehdari and Sothcott (2003) compiled rock-fluid interac-
 tions that explain the rock shear modulus (μ) variability with fluids.
 They define rock weakening when $\mu_{\text{saturated}} < \mu_{\text{dry}}$, and strengthening
 for $\mu_{\text{saturated}} > \mu_{\text{dry}}$. Cardona et al. (2001), based on work from Brown
 and Korringa (1975) show that for an anisotropic rock, the vertically
 propagating shear waves are sensitive to the compressibility of the
 saturating fluid. However, our rocks are largely isotropic at the core
 scale, although they might be anisotropic at field scale. Therefore, in
 our work, we will focus on the rock-fluid interactions that are re-
 sponsible for rock shear modulus changes.

Data examples of shear modulus sensitivity to fluids and possible explanations

Figure 6 shows the rock shear modulus for sample *C* at seismic
 and ultrasonic frequencies when dry and brine saturated. Error bars
 represent one standard deviation of the shear modulus. Two main ob-
 servations are to be drawn from Figure 6. First, the rock shear modu-
 lus can either weaken or strengthen upon brine fluid saturation com-
 pared to the dry rock. At 100 Hz we observe shear modulus weaken-
 ing from dry to wet, while for 0.8 MHz data the shear modulus
 strengthens when brine fills the pore space. This implies that more
 than one rock-fluid mechanism is active.

Second, for the 100 Hz frequency measurements, the shear modu-
 lus weakens more for low- than for high-differential pressures. Our
 measurements are performed going from high- to low-differential
 pressures (unloading cycle). After the experiment with brine satura-
 tion reached 3.5 MPa, we increased the differential pressure again
 for three pressure stages (circles in Figure 6). Observe that the rock
 shear modulus sensitivity to brine saturation for both 100 Hz and
 0.8 MHz is repeatable; thus, the shear modulus weakening is not af-
 fected by hysteresis. This reversible weakening or strengthening of
 the frame is likely associated with the opening and closing of com-
 pliant pores or cracks. Some of these cracks are intrinsic to the rock,
 while others might have been induced while drilling or coring. Other
 samples with significant shear modulus weakening show similar
 pressure dependence to sample *C*.

Figure 7 compares the dry- and brine-saturated rock shear modu-
 lus for all samples for 100 Hz at 3.5 and at 31 MPa differential pres-
 sure. The solid line indicates equal dry- and brine-saturated shear

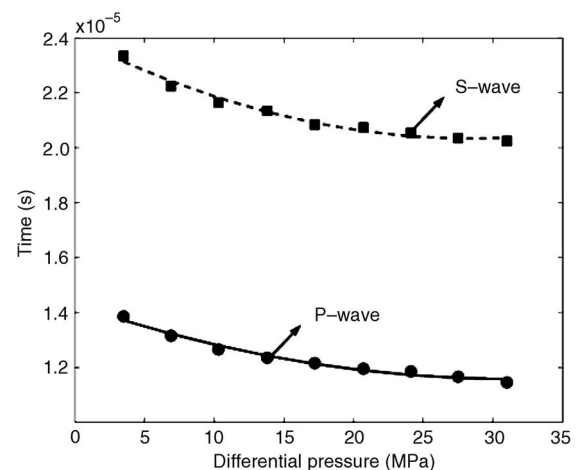


Figure 5. Second-order polynomial fit to ultrasonic travel times as a function of differential pressure for sample *D* under butane saturation.

383 modulus. Most samples have a rock shear modulus around 10 MPa.
 384 This cluster of data corresponds to samples with high porosity
 385 (24–35%), while the low-porosity samples have a shear modulus
 386 larger than 15 MPa. The error bars of the shear modulus (one stan-
 387 dard deviation) are within the size of the marker. Observe that at low-
 388 differential pressures (3.5 MPa) all samples show shear modulus
 389 weakening, while at higher pressures (31 MPa), shear modulus
 390 weakening is still present but less significantly than for low pressure
 391 (see also Figure 6).

392 Most samples at ultrasonic frequency and at both 3.5 and 31 MPa
 393 differential pressure show neither weakening nor strengthening of
 394 the rock shear modulus within the data uncertainty (Figure 8). Weak-
 395 ening is observed in samples *B* and *D*, but less than for seismic fre-
 396 quency (Figure 7).

397 When we compare Figures 7 and 8, the shear modulus for brine-
 398 saturated rock at ultrasonic frequency is greater than for seismic fre-
 399 quency. This *comparative* strengthening could describe modulus
 400 dispersion as a result, for example, of global- and squirt-fluid flow in
 401 the pore space. However, for samples *B* and *D*, the chemical soften-
 402 ing of the rock could be dominating over the modulus dispersion. Al-
 403 ternatively, our ultrasonic-wave velocity represents the fastest path
 404 (stiffest area in the rock). If the chemical weakening is occurring in
 405 an isolated area of the sample, the stress-strain experiment measures
 406 the effective rock deformation (frame softening), while the ultrason-
 407 ic wave will avoid this area and propagate in the unperturbed rock.

408 We also saturated the carbonate rocks with butane, a highly compress-
 409 ible, light hydrocarbon (in liquid phase at our elevated pore pres-
 410 sures). The sensitivity of the rock shear modulus to this fluid is
 411 much less than for brine (Figure 9).

412 We can now examine what are the possible weakening and
 413 strengthening mechanisms acting on our carbonate rocks based on
 414 the work of Khazanehdari and Sothcott (2003). They compiled sev-
 415 eral mechanisms that can cause the shear modulus to either weaken
 416 or strengthen when a fluid contacts the solid matrix.

417 Pores and microfractures create surface area in a rock. Surface-

energy reduction (Murphy et al., 1986; Tutuncu and Sharma, 1992) 418
 and subcritical crack-growth (Atkinson, 1984) mechanisms relate to 419
 the amount of surface area in a porous rock. Compliant pores and mi- 420
 crofractures are observed in our samples from thin sections. We also 421
 know, from the modulus as a function of differential pressure, that 422
 compliant pores and microfractures open, increasing the surface 423
 area, as the differential pressure decreases (Figure 6). For our sam- 424
 ples, open low aspect ratio pores might exhibit growth as well as 425
 breakage of solid bounds due to interaction with brine. These two 426
 mechanisms, acting on our carbonate samples, are consistent with 427
 the fact that a nonpolar fluid, such as butane, saturating the rock, 428
 does not show significant shear modulus variation (Figure 9). Another 429
 rock-fluid mechanism such as viscous-coupling (Bourbié et al., 430
 1987), is probably not the cause of shear modulus variability in car- 431
 bonates because the sensitivity to brine is large while it is not signifi- 432
 cant for liquid butane, with both fluids having similar and low vis- 433
 cosities (0.2 cP for liquid butane and 1 cP for brine). Dissolution of 434
 carbonate minerals could also be occurring. Dissolution of calcite 435
 and dolomite minerals depends on the pH of the fluid, temperature, 436
 and the reaction order of the cations (Ca, Mg, Ba) which control the 437
 dissolution rate of carbonate minerals (Chou et al., 1989). 438

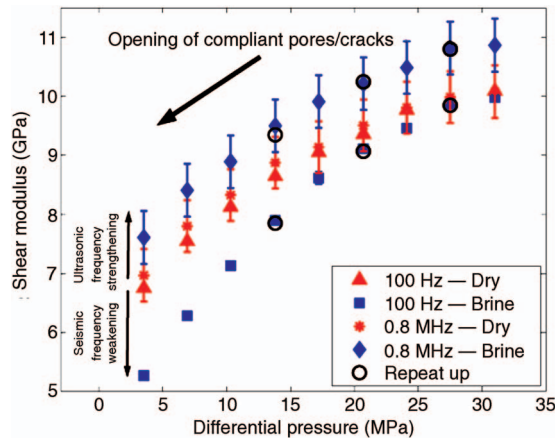


Figure 6. Sample *C*, showing shear modulus weakening and strengthening at seismic and ultrasonic frequencies respectively. Measurements are performed from high- to low-differential pressures. Circles represent repeated differential pressures going from low- to high-differential pressures after the initial unloading cycle was finalized. Note that as we decrease the differential pressure, more compliant pores and cracks open. Error bars are one standard deviation (one σ for seismic frequency data is contained in the size of the symbol).

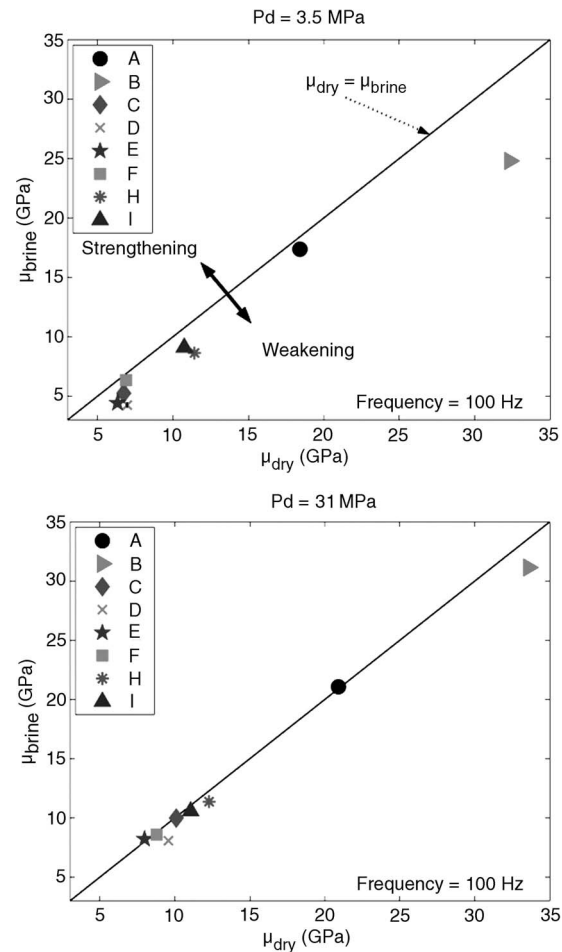


Figure 7. Shear modulus weakening in carbonate samples resulting from dry to brine saturation at seismic frequency (100 Hz) for differential pressures of 3.5 and 31 MPa. Error bars, representing one standard deviation, are within the size of the marker for most samples.

439 By acquiring data at seismic and ultrasonic frequencies, we observe
 440 evidence of at least three mechanisms for which the shear modulus
 441 weakens (surface-energy reduction and crack growth) or strengthens (modulus dispersion). Changes in shear modulus could
 442 be observed from seismic time-lapse data, especially in the presence
 443 of compliant pores and polar fluids such as water. When injecting
 444 water into an oil reservoir, the nature of this polar fluid, its viscosity,
 445 pressure, temperature, etc. will likely interact with the rock solid
 446 phases creating weakening or strengthening of the shear modulus
 447 (and maybe in some cases the bulk modulus) compared to the original
 448 fluid saturation.
 449

450 Also, when logging data is available in a field, the analysis has to
 451 consider that modulus dispersion can be significant and should be
 452 taken with care if compared to seismic data. Log data will fall in between
 453 our measured frequency ranges (~10 KHz). Having knowledge of the characteristic
 454 frequency (f_c) might help the interpretation of log data. The f_c separates the behavior for relaxed and unrelaxed
 455 fluids. If $f_{log} < f_c$ and we have compliant pores, we could observe
 456 weakening of the shear modulus upon water saturation. On the other hand, if the $f_{log} > f_c$, strengthening of the shear modulus
 457 might be observed. Sharma et al. (2006) compiled results for the shear
 458 modulus change from dry to water saturation from several authors.
 459
 460

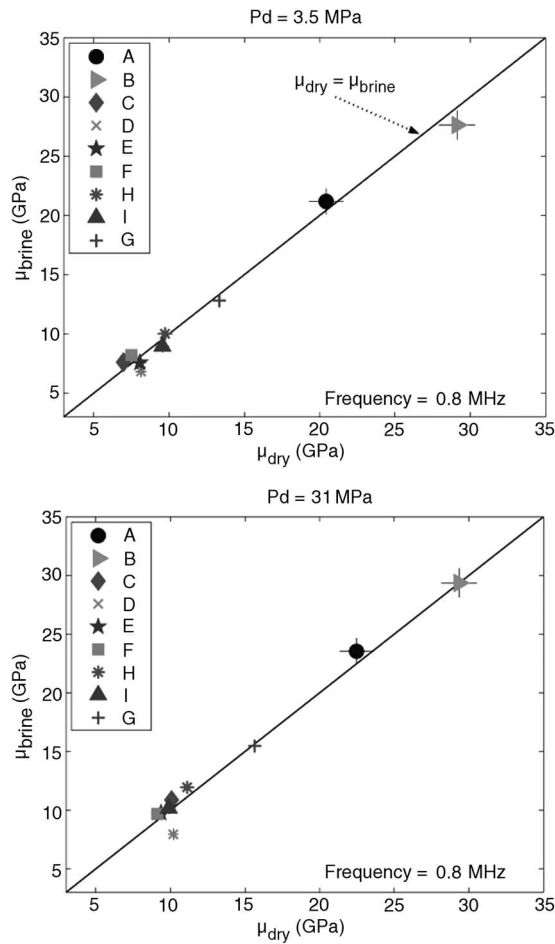


Figure 8. Carbonate samples showing that the shear modulus remains almost constant from dry to brine saturation at ultrasonic frequency for differential pressures of 3.5 and 31 MPa. Error bars, representing one standard deviation, are within the size of the marker for most samples.

In this study, the shear modulus strengthens at ultrasonic frequencies and weakens for sonic frequencies (~10 KHz) for data by Lucet (1989). This observation is in agreement with our observations on shear modulus change from seismic to ultrasonic frequencies.

GASSMANN'S FLUID SUBSTITUTION

We introduced Gassmann's theory with its assumptions, and in this section we compare and analyze the computed saturated bulk modulus, using Gassmann's theory, to the measured rock bulk modulus. Our experimental setting for seismic-frequency data acquisition lets us acquire data when the fluid is at equilibrium. The pore pressure is held constant, thus the fluid modulus is 0.5 GPa for butane, and 3.4 GPa for brine.

Figure 10 compares the bulk modulus, calculated using the Gassmann theory, to the measured bulk modulus for butane-saturated carbonates at frequencies of 100 Hz and 0.8 MHz, and at a differential pressure of 31 MPa. The solid line represents the case where the butane-substituted modulus, predicted by Gassmann's theory, and the measured bulk modulus are equal. Error bars represent one standard deviation for the bulk modulus. Gassmann's theory is correctly pre-

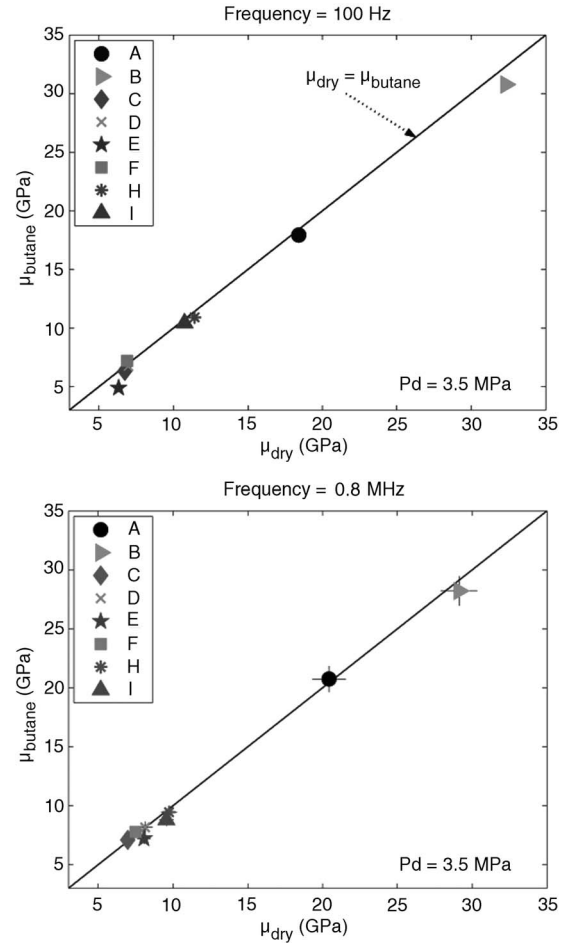


Figure 9. Carbonate samples showing little shear modulus weakening and strengthening resulting from dry to butane saturation compared to the dry-brine saturation case. Both plots are at a differential pressure of 3.5 MPa for seismic and ultrasonic frequencies. Error bars, representing one standard deviation, are within the marker size for most samples.

480 dicting the observed butane-saturated modulus for our carbonate
 481 samples, partly because the influence of butane on the rock bulk
 482 modulus is not large. Butane is a highly compressible fluid, thus the
 483 fluid influence on rock compressibility is not significantly different
 484 from the dry rock (see Figure 2).

485 For brine saturation, Gassmann-calculated and measured bulk
 486 moduli m at 100 Hz and 0.8 MHz, and at differential pressures of 3.5
 487 and 31 MPa m are compared in Figures 11 and 12 respectively. The
 488 solid line represents the case where the fluid-substituted and measured
 489 moduli are equal. Error bars represent one standard deviation
 490 for the bulk modulus. Observe that some samples match the predic-
 491 tions well, while others do not.

492 In Figure 11, at a frequency of 100 Hz, none of the predictions fit
 493 the observed bulk modulus within the associate uncertainty, while at
 494 0.8 MHz, for the same differential pressure of 3.5 MPa, the fit to the
 495 predicted bulk modulus is better. At low-differential pressure and at
 496 100 Hz, the bulk moduli for all of the samples but F are overpredic-
 497 ted by Gassmann's theory. We observe shear modulus weakening for
 498 all samples (and the least for sample F , Figure 7), therefore if the
 499 rock frame has weakened in the presence of brine, so could the bulk
 500 modulus, m a factor not accounted for in Gassmann's theory. There-

501 fore, the overprediction of the bulk modulus by Gassmann's theory
 502 at low-differential pressure is probably because the rock frame has
 503 been altered (softened).

504 The bulk modulus is underpredicted for 100 Hz, yet it is well pre-
 505 dicted at 0.8 MHz (Figure 11). This is largely a result of modulus
 506 dispersion. Remember that Gassmann's theory estimates the saturat-
 507 ed modulus for low frequencies. Gassmann's theory uses the bulk
 508 modulus of the dry rock, which is not dispersive, to predict the sat-
 509 urated rock modulus. However, modulus dispersion exists in most of
 510 our brine-saturated carbonates (see Figure 2). This bulk modulus
 511 dispersion is evidenced in the shifting of data points in Figure 11 as
 512 the frequency increases from 100 Hz to 0.8 MHz. The bulk modulus
 513 *shift* occurs parallel to the x-axis (measured saturated bulk modu-
 514 lus). This bulk modulus dispersion at ultrasonic frequency can lead
 515 to errors when comparing ultrasonic to seismic data. Thus, a better fit
 516 at ultrasonic frequency might be somewhat of a paradox on Gas-
 517 ssmann's-theory applicability for carbonates.

518 At a differential pressure of 31 MPa (Figure 12), the 100 Hz data
 519 shows that the bulk modulus of four brine-saturated carbonates (B ,
 520 E , I , and H) is predicted well by Gassmann's theory. The bulk moduli
 521 for samples A and C are largely overpredicted by Gassmann's theo-

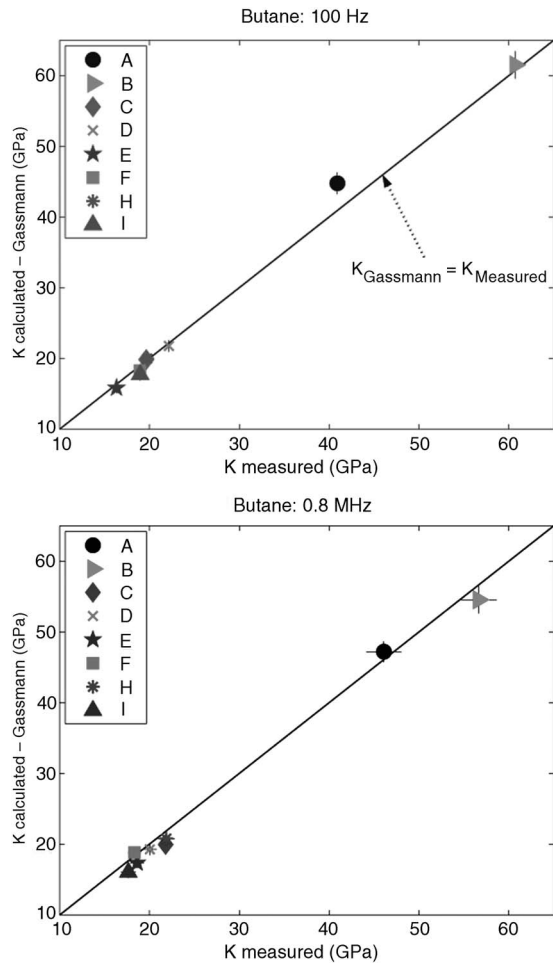


Figure 10. Butane-saturated bulk moduli measured and estimated with Gassmann's theory for 100 Hz and 0.8 MHz at 31 MPa differential pressure. Solid line represents equal measured and estimated bulk modulus. Error bars are one standard deviation of the bulk modulus.

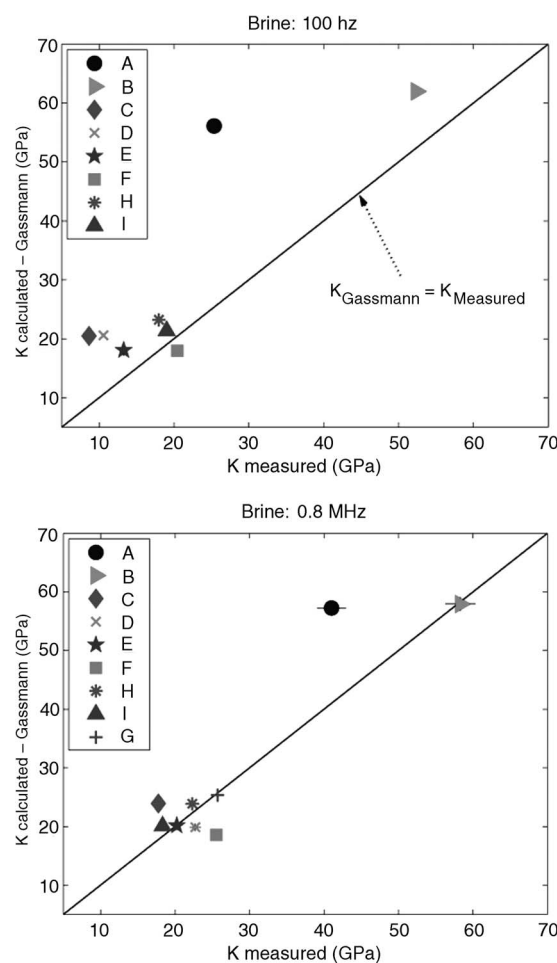


Figure 11. Brine-saturated bulk moduli measured and estimated with Gassmann's theory for 100 Hz and 0.8 MHz at 3.5 MPa differential pressure. Solid line represents equal measured and estimated bulk modulus. Error bars are one standard deviation of the bulk modulus.

522 ry. Samples *A* and *C* have the highest content of non-calcareous minerals, especially clay. We ignore that softening of clays is a possible
 523 mechanism for elastic moduli weakening for most of our samples.
 524 However, that $K_{Measured}$ is significantly less than $K_{Gassmann}$ for samples
 525 *A* and *C* is possibly related to frame (clay) weakening in the presence
 526 of brine.
 527

528 We focus now on data at 100 Hz, where frequencies are low enough that we expect the fluid-pressure gradients are zero, as Gassmann's theory requires. Still, at high differential pressure, we observe that some samples are well predicted by Gassmann's theory, while others are not. So where can this difference come from? On one hand, we have observed rock shear modulus sensitivity to brine saturation. On the other hand, for low-differential pressures, we expect to have open compliant pores or cracks. Gassmann's equations are derived without assuming any specific pore geometry, and can be applied to any pore type as long as the assumptions for Gassmann's theory are satisfied, i.e. pore pressure is in equilibrium. The mismatch between observed and Gassmann-predicted bulk modulus could relate to differences in pore type creating pressure gradients or chemical reactions which violate Gassmann's assumptions. Therefore, samples yielding better predictions by Gassmann's theory

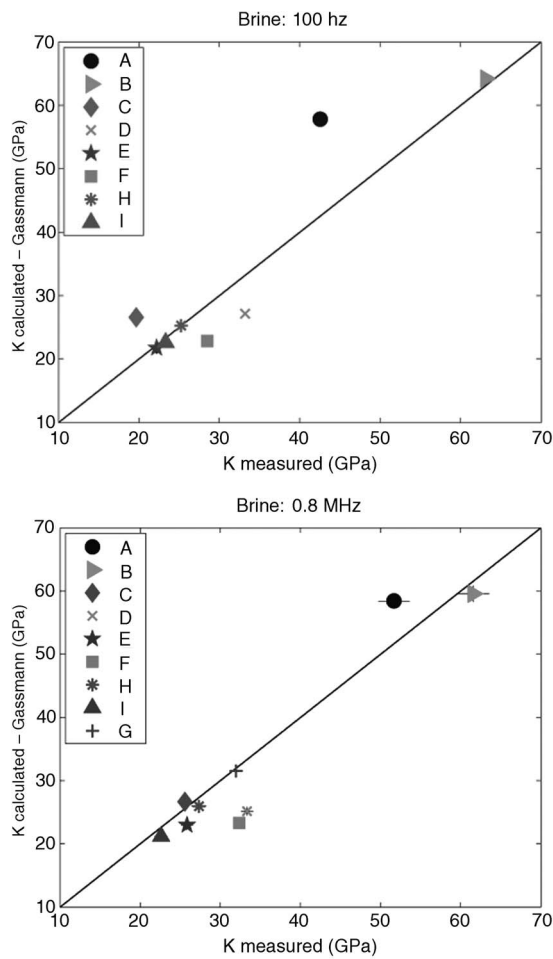


Figure 12. Brine-saturated bulk moduli measured and estimated with Gassmann's theory for 100 Hz and 0.8 MHz at 31 MPa differential pressure. Solid line represents equal measured and estimated bulk moduli. Error bars are one standard deviation of the bulk modulus.

543 might be explained through the dependence of bulk modulus with
 544 differential pressure. Figure 13 plots the bulk modulus of brine-saturated
 545 carbonates as a function of differential pressure. The anomalous
 546 behavior of sample *D* at 20.7 MPa is due to a small gas leak into
 547 the rock when the sample was saturated with brine. This dramatically
 548 lowered the bulk modulus of sample *D* at low frequencies for pressures
 549 lower than 20.7 MPa. In Figure 13, we observe a consistent
 550 linear behavior of the bulk modulus with differential pressure from
 551 the Hertz-Mindlin model: $K = mP^{1/3}$ (Mavko et al., 1998), where the
 552 slopes (m) of the linear trends are different for different rocks. Higher
 553 slopes mean larger dependence on differential pressure, indicating the
 554 existence of compliant pores or microcracks. Table 2 compares Gassmann's
 555 predictability, shear modulus weakening, mineralogy, and pressure effect
 556 on all samples at 100 Hz. Gassmann's predictability and shear modulus
 557 weakening are reported for the highest differential pressure reached at
 558 31 MPa. The pressure effect is measured by the slope of the linear
 559 dependence (m) of the bulk modulus (Figure 13).
 560

561 There seems to be no correlation between the shear modulus
 562 weakening and the observed match between measured and computed
 563 bulk moduli for brine-saturated carbonates at high differential
 564 pressure (Table 2). For example, both samples *B* and *D* show significant
 565 shear modulus weakening at 31 MPa differential pressure; still sample
 566 *B* is well predicted by Gassmann's theory while sample *D* is not. It
 567 might seem confusing that although Gassmann's assumption that the
 568 rock frame stays unaltered by the fluid is violated for some samples,
 569 the measured brine-saturated bulk modulus is well predicted by
 570 Gassmann's theory for these samples. A likely reason for this is
 571 because the increase in bulk modulus, in absolute percent from dry to
 572 brine saturation (35% in average), is more significant than the shear
 573 modulus weakening, in absolute percent (6% in average).
 574

575 Examining the pressure dependence, the saturated bulk modulus
 576 for samples with lower slopes (*B*, *E*, *H* and *I*) is well predicted by
 577 Gassmann's theory. Low slopes mean the sample has less compliant
 578 pores or cracks. Samples *A*, *C* and *D* have high slopes, and Gassmann's
 579 theory is not predicting the observed saturated bulk modulus. Sample
 580 *F* has an intermediate slope, but the saturated bulk modulus is not
 581 well predicted by Gassmann's theory. For sample *F*, the bulk modulus
 582 as a function of pressure is less smooth than for other samples, leading
 583 to a higher variance in the slope calculation. As pre-

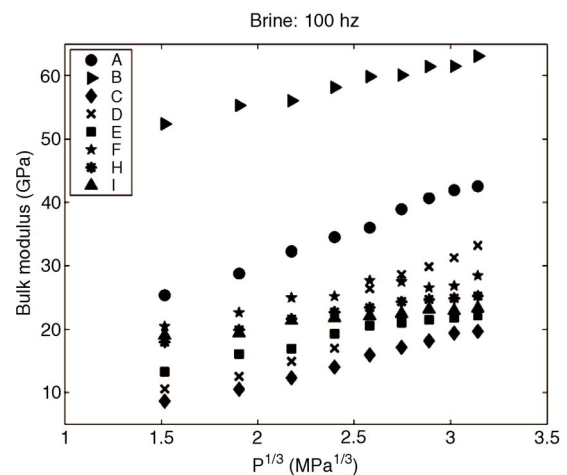


Figure 13. Bulk modulus for carbonates with brine saturation as a function of differential pressure ($P^{1/3}$) for 100 Hz.

Table 2. Gassmann's theory applicability correlated with shear-modulus weakening and bulk-modulus dependence with pressure (slopes of Figure 13). Gassmann and shear-modulus analysis corresponds to 100 Hz at a differential pressure of 31 MPa. X means the statement is true. Dominant mineralogy: C=calcite, D=dolomite. Note correspondence of good Gassmann's theory fit with low-pressure dependence (*m*).

SAMPLES	A	B	C	D	E	F	H	I
Gassmann's theory fits		X			X		X	X
Shear modulus weakening		X		X			X	
Bulk modulus vs. pressure (<i>m</i>)	11.8	5.6	7.9	11.2	5.2	5.4	4.5	3.2
Mineralogy	C	D	C	C	C	C	D	D

583 viously mentioned, our experimental setup could not quite reach the
 584 differential pressure of the reservoir at 34.5 MPa. This could result
 585 in some compliant pores still being open at these pressures. From
 586 this we conclude that open compliant pores are a possible factor af-
 587 fecting the mismatch between observed and predicted bulk modulus.
 588 Samples *B*, *H* and *I* are dolomites, but we do not have enough statisti-
 589 cal data to make correlations with rock grain density. Nevertheless,
 590 these dolomite samples have high porosity and permeability *m* prob-
 591 ably satisfying Gassmann's assumption on pore connectivity and
 592 fluid distribution in the porous space.

593 From our observations, carbonates with round pores, vugs or mi-
 594 critic textures are well predicted by Gassmann's theory for low fre-
 595 quencies. Even at reservoir pressures, open compliant pores or
 596 cracks might be present at reservoir in-situ conditions. In this case,
 597 an anisotropic fluid-substitution theory, such as that of Brown and
 598 Korringa (1975), is perhaps more appropriate. However, knowledge
 599 of the anisotropic symmetry, with all of the stiffness coefficients of
 600 the rock and the pore-space compressibility, are required for this the-
 601 ory. Using additional parameters might allow one to fit the data bet-
 602 ter, but the estimated parameter could not be realistic or representa-
 603 tive of the rock.

604 **CONCLUSIONS**

605 We present data over a large range of frequencies and under vary-
 606 ing saturation and pressure conditions to investigate the applicabili-
 607 ty of Gassmann's theory for our carbonate data set. We observe that
 608 the rock shear modulus is sensitive to brine saturation, especially at
 609 seismic frequencies. Weakening of the solid matrix occurs possibly
 610 due to surface energy loss and/or subcritical crack growth in compli-
 611 ant pores, mostly at low-differential pressures. These mechanisms
 612 violate an assumption of Gassmann's theory that the fluid does not
 613 influence the solid matrix of the rock. However, we find no positive
 614 correlation between the rock shear modulus weakening and the fail-
 615 ure of Gassmann's theory to predict the saturated bulk modulus at
 616 seismic frequencies. We do find that the brine-saturated bulk modu-
 617 lus, for carbonates with small differential pressure dependence
 618 (round pores or vugs), is well predicted by Gassmann at seismic fre-
 619 quencies, while for carbonates strongly influenced by pressure
 620 (compliant pores or microcracks), Gassmann's theory does not
 621 match the observations. Therefore, knowledge of the reservoir pore-

space geometry can aid in the understanding and applicability of
 Gassmann's theory.

Predicting the saturated bulk modulus at ultrasonic frequencies
 violates Gassmann's low-frequency assumption. Nevertheless, we
 test our carbonate samples at ultrasonic frequencies to show the role
 of modulus dispersion. For some of our samples, the measured and
 Gassmann-calculated bulk moduli at ultrasonic frequencies show
 better agreement compared to seismic frequencies. This match is ap-
 parent, resulting from bulk modulus dispersion which we observe in
 our carbonates when saturated with brine. We also observe shear
 modulus dispersion. Little change from dry to brine saturation is
 present in the rock shear modulus at ultrasonic frequencies, but this
 modulus is always higher than the shear modulus obtained at seismic
 frequencies. This increase could be a result of dispersion or a prefer-
 ential propagation path, which avoids altered (weakened) sections in
 the saturated rocks. Although our conclusions are based on samples
 with different texture and mineralogy, we must be careful to general-
 ize these results to all carbonate rocks.

Our observations are applicable particularly to the analysis of
 time-lapse data. Ultrasonic laboratory data is used in some cases to
 calibrate time-lapse seismic reflection data. We should be aware that
 bulk modulus in carbonate rocks can have significant dispersion af-
 fecting the applicability of Gassmann's fluid-substitution theory at
 ultrasonic frequencies (and maybe at log frequencies). Also, when
 water or brine replaces a nonpolar fluid such as oil, shear modulus
 weakening can be observed in the field. Brine of different salinity
 and temperature injected in an aquifer to enhance production might
 change the solid frame, causing variation in the moduli of the rocks.

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