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ABSTRACT

As part of our study on “Relationships between seismic properties and rock microstructure”, we have studied

1. Elastic properties of clay minerals using Pulse Transmission experiments. We show measurements of elastic moduli and strain in clay minerals.

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INTRODUCTION

In this quarter, we submit results of our research on measurements of clay modulus using pulse transmission experiments and measurements of seismic properties of unconsolidated sediments (clays) at very low effective pressures. One paper has been accepted for publication on this work. This report presents the preprint of our research relevant to this project on correlation between clay content and seismic properties reservoir rocks.

PAPER 1

Vanorio, T., Prasad, M., and Nur, A.: Elastic Properties of Dry Clay Mineral Aggregates, Suspensions and Sandstones, to appear in Geophys. Jour. Intl.

The presence of clay minerals can alter the elastic behavior of rocks significantly. Although clay minerals are common in sedimentary formations and seismic measurements are our main tools to study subsurface lithologies, measurements of elastic properties of clay minerals have proven difficult. Theoretical values for bulk modulus of clay are reported between 20 – 50 GPa. The only measurement of Young's modulus in a clay mineral using Atomic Force Acoustic Microscopy (AFAM) gave a much lower value of 6.2 GPa. This study has concentrated on using independent experimental methods to measure the elastic moduli of clay minerals as functions of pressure and saturation. First, ultrasonic P- and S-waves velocities were measured as functions of hydrostatic pressure in cold-pressed clay aggregates with porosity and grain density ranging from 4 to 43% and 2.13 to 2.83 g cm⁻³, respectively. In the second experiment, P- and S-waves velocities in clay powders were measured under uniaxial stresses compaction. In the third experiment, P-wave velocity and attenuation in a kaolinite-water suspension with clay concentrations between 0 – 60% were measured at ambient conditions. Our elastic moduli measurements of kaolinite, montmorillonite, and smectite are consistent for all experiments and with reported AFAM measurements on a nanometer scale. The bulk (K) modulus values lie between 6 and 12 GPa and shear (m) modulus values vary between 4 and 6 GPa. A comparison is made between accuracy of velocity prediction in shaley sandstones and clay-water and clay-sand mixtures using the values measured in this study and those from theoretical models. Using $K_s=12$ GPa and $m_s=6$ GPa from this study, the models give a much better prediction both of experimental velocity reduction due to increase in clay content in sandstones and velocity measurements in a kaolinite water suspension.

Paper 1: Total of nine figures in paper

Elastic Properties of Dry Clay Mineral Aggregates, Suspensions and Sandstones

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SUMMARY

The presence of clay minerals can alter the elastic behavior of rocks significantly. Although clay minerals are common in sedimentary formations and seismic measurements are our main tools to study subsurface lithologies, measurements of elastic properties of clay minerals have proven difficult. Theoretical values for bulk modulus of clay are reported between 20 – 50 GPa. The only measurement of Young's modulus in a clay mineral using Atomic Force Acoustic Microscopy (AFAM) gave a much lower value of 6.2 GPa. This study has concentrated on using independent experimental methods to measure the elastic moduli of clay minerals as functions of pressure and saturation. First, ultrasonic P- and S-waves velocities were measured as functions of hydrostatic pressure in cold-pressed clay aggregates with porosity and grain density ranging from 4 to 43% and 2.13 to 2.83 g cm⁻³, respectively. In the second experiment, P- and S-waves velocities in clay powders were measured under uniaxial stresses compaction. In the third experiment, P-wave velocity and attenuation in a kaolinite-water suspension with clay concentrations between 0 – 60% were measured at ambient conditions. Our elastic moduli measurements of kaolinite, montmorillonite, and smectite are consistent for all experiments and with reported AFAM measurements on a nanometer scale. The bulk (K) modulus values lie between 6 and 12 GPa and shear (μ) modulus values vary between 4 and 6 GPa. A comparison is made between accuracy of velocity prediction in shaley sandstones and clay-water and clay-sand mixtures using the values measured in this study and those from theoretical models. Using $K_s=12$ GPa and $\mu_s=6$ GPa from this study, the models give a much better prediction both of experimental velocity reduction due to increase in clay content in sandstones and velocity measurements in a kaolinite water suspension.

Keywords: acoustic velocities, elastic moduli, clay minerals, porosity

INTRODUCTION

Elastic properties of clay minerals are of great interest for exploration and characterization of shaley formations. Knowledge about elastic moduli of clay minerals is required because: 1) clay minerals are found in most sedimentary environments; 2) clay mineral transitions are considered as important factors in seismogenic zones; 3) seismic interpretation and modeling seismic response requires knowledge on how the presence of clay changes physical properties of rocks.

Laboratory data from several investigators (Tosaya and Nur, 1982; Tosaya, 1982; Kowallis *et al.*, 1984; Han, 1986; Klimentos, 1991) report a systematic decrease of P- and S- wave velocity with increasing clay content in both well and poorly consolidated sediments. However, the empirical relations derived from these measurements are restricted to specific lithologies and thus resist generalization. On the other hand, the use of deterministic models to establishing porosity-velocity relations in shaley sandstones requires knowledge of input parameters such as elastic moduli of solid clay phase.

Elastic properties of clay minerals are almost unknown mainly because of the difficulty presented by their intrinsic properties. Their small grain size makes it impossible to isolate an individual crystal of clay large enough to measure acoustic properties; reactions with organic polar molecules (Theng, 1974) affects handling and clay structure; and low permeability makes saturation difficult. So far the effective elastic properties of clays have been derived either by theoretical computation (Alexandrov and Ryzhova, 1961; Berge and Berryman, 1995; Katahara, 1996), by a combination of theoretical and experimental investigations on clay-epoxy mixtures (Wang *et al.*, 2001),

or by empirical extrapolations from measurements on shales (Tosaya, 1982; Castagna *et al.*, 1985; Han, 1986). These derived values of clay moduli show little agreement. The values reported by Katahara (1996) and Wang *et al.*, (2001) (ca. 50 GPa for bulk modulus, K and 20 GPa for shear modulus, μ) are higher than those extrapolated (ca. 20 GPa for K and 7 GPa for μ) from both laboratory (Castagna *et al.*, 1985; Han, 1986; Tosaya, 1982) and well log measurements in shales and laminated shaley-sands (Eastwood and Castagna, 1987). Katahara (1996) explained this discrepancy by acoustic anisotropy: in shaley beds, clay particles tend to align parallel to bedding during compaction. Using theoretical models of shaley sandstones, Berge and Berryman (1995) have shown that bulk modulus of clay should be around 10-12 GPa. Only one experimental measurement exists on pure clay minerals: Prasad *et al.* (2002) have reported measurements of Young's modulus on clay particles using Atomic Force Acoustic Microscopy. Their measured value of Young's modulus for dickite is 6.2 GPa.

We have made direct measurements of the elastic properties of clay minerals by designing experiments that took into account factors affecting clay structures. We used three independent experimental set-ups: 1) a method of obtaining dry clay aggregates having different porosities on which P- and S-velocity (V_p , V_s , respectively) measurements were made as functions of hydrostatic pressure; 2) V_p and V_s measurements on clay powder as functions of uniaxial stress; 3) P- velocity and -attenuation (V_p and Q_p , respectively) measurements on water-clay suspension as functions of clay content.

The measurements of elastic moduli for solid clay phase from all experiments are consistent with each other. In order to verify the reliability of results, the measured

moduli values were used in effective medium and granular porous media models and compared to preexisting data on shaley sandstones (Klimentos, 1991; Han, 1986; Tosaya, 1982). We demonstrate that our measured values of the elastic moduli for clay can be used to predict velocity data in saturated kaolinite samples (Yin, 1993), kaolinite–water suspensions (this study) and shaley sandstones (Klimentos, 1991; Han, 1986; Tosaya, 1982).

2 EXPERIMENTAL PROCEDURES AND METHODS

2.1. Collection of Clay Samples

Samples used in this study were prepared from clay powders obtained from the repository of the Clay Minerals Society. Clay samples included: Kaolinite (KGa-1b, reported in the paper as Ka1), Ca-Montmorillonite (STx-1, reported as Ca-Mt), Na-Montmorillonite (SWy-2, reported as Na-Mt), Illite (IMt1, reported as Imt), Smectite (SWa-1, reported as Sm), and Chlorite (CCa-2, reported as Ch).

2.2. Methods

Our methods of measuring elastic moduli of solid clays were chosen taking into account the various factors affecting clay structures. Brace *et al.* (1969) and Chung (1979) have described a hot-pressing method to determine elastic properties of some mineral powders. This method cannot be used for clays because they are sensitive to temperature and pressure. As temperature increases, clays first dehydrate and then dehydroxylate changing, respectively, their adsorbed water content and their mineral structure. The dehydration temperature depends on pressure (Colten, 1987; Koster Van Groos and Guggenheim, 1984). Chemical reagents cannot be used for sample preparation because some clay minerals change structure due to reaction with polar compounds.

These reactions can be exothermic and the temperature may rise to such a level as to overheat the clay specimen (Theng, 1974; Newman, 1987). The effects of reactions on clay minerals depend largely on their structure (Theng, 1974). The basal spacing of the $\text{Si}(\text{O},\text{OH})_4$ -tetrahedra (T) and $\text{M}_{2-3}(\text{OH})_6$ -octahedra (O) layers (where M is either a divalent or a trivalent cation) as well as size, valence, and charge of the embedded exchangeable cations profoundly influence adsorption of polar molecules other than water. For example, kaolinite shows a fully collapsed structure that is wanting either in water molecules or in exchangeable cations or both. In these structures, intercalation of polar organic liquids or gases is quite complex and adsorption occurs predominantly on the external crystal surfaces (Theng, 1974). On the other hand, smectite-type minerals, which host both exchangeable cations and water interlayers, adsorb polar organic molecules by replacing their water interlayers. During the internal adsorption, the organic compound competes with water for the same sites around the exchangeable cation. The removal and replacement of the water interlayer can be so invasive to provoke dissociation of clay layers (Theng, 1974).

An understanding on how these factors affect acoustic measurements is lacking. Since all the above-mentioned effects alter the clay structure, we expect an accompanying change in elastic properties as well. To eliminate these secondary effects, we used the cold-pressing method in which measurements are conducted on pure clay powders pressed at ambient room temperatures. Relatively low-pressure conditions (up to 20 MPa) ensured that the applied pressures did not promote dehydration of the clay minerals. Similarly, in the suspension experiment, a KCl solution was used with kaolinite to limit

the effects of adsorption of polar water molecules and the cation exchange capacity of the clay.

2.2.1 Porosity and Grain Density Determination

Grain density of the clay powders was measured using a pycnometer. To avoid trapped air produced by clay flocculation, we used sodium hexametaphosphate in distilled water (40 g of solute/liter) as dispersive agent (ASTM D854-92, 1992). For the cold-pressed aggregate samples, porosity, bulk- and grain- densities were measured at room P-T conditions with a Helium porosimeter (error of measurements about 1%).

2.2.2 Cold-Pressing Experiment

Samples preparation: this set-up was designed to make clay aggregate samples from the powders described in Section 2.1. These samples were used for measurements of V_p and V_s as functions of hydrostatic pressure. The equipment consists of a split steel cube with a cylindrical cavity (Figure 1). Two pistons on either side of this cavity are used to apply uniaxial stress on a powder placed in the cavity. Porous stones coupled to filter paper on either end prevented the samples from bonding to the endplates during the cold-pressing procedure. The split steel cube allows sample recovery without applying additional stress. Powders were cold-pressed at 15 MPa for 1, 7, and 10 days to obtain samples of different porosity. Porosity, density, and acoustic properties were measured on these samples at ambient conditions and at different confining pressure (up to 20 MPa).

Acoustic measurements: A complete description of the experimental set-up used in this study can be found in Prasad et al. (1997) and Vanorio et al. (2002). Measurements were performed by increasing confining pressure up to 20 MPa with a pressure interval of 1MPa. During down cycle, measurements were taken with a pressure interval of ≈ 5 MPa.

Three linear potentiometers were used to measure length changes of the samples as a function of stress. The length change was directly related to changes in porosity by assuming that pore collapse was the main cause of strain. This allowed computation of porosity change with pressure using initial porosity, grain density, and length change. V_p and V_s were measured at each pressure step. Travel-time was measured after digitizing each trace with 1024 points at a time sweep of 5 μ s, thus allowing a time resolution of about 5 ns or about 0.2% error in velocity. Actual error in velocity measurement is estimated to be around 1% due to operator error in picking first arrival time. The system delay time was measured by taking head-to-head time at 2 MPa. The travel-time calibration was confirmed by measuring an aluminum sample at different pressures.

2.2.3 Uniaxial Stress Experiment

Samples preparation: clay powder of kaolinite (KGa-1b), Na-montmorillonite (SWy-2), and Ca-montmorillonite (STx-1) were used for this experiment. The cold-pressing set-up was altered to allow the simultaneous measurement of acoustic velocities during the uniaxial stress compaction of clay powders. PZT-crystals with principal frequency of 1 MHz mounted on the piston endplates were used to generate P- and S-waves. A high-viscosity bonding medium (Panamterics SWC) was used to bond the endplates to the sample. Acoustic isolation from steel was achieved by jacketing the samples with rubber tubing.

Acoustic Measurements: The experimental setup for the uniaxial pressure tests consisted of a digital oscilloscope (Tektronix TDS 420A) and a pulse generator (Panametrics 5052 PR). Measurements were performed by increasing pressure up to 20 MPa with a variable pressure interval from 2.5 to 5 MPa. A caliper was used to measure length changes of the

samples as a function of stress (precision = $\pm$). The length measurements were made at eight positions around the plate in order to detect possible sample tilting. Computations of both porosity change and travel- time were made as described in Section 2.2.2. In this experiment, porosities might be underestimated due to deformation of rubber jacket. However, comparison with our other results and the modeling in Section 4 show this deformation to be minimal. This assumption was further tested by using water sample in the uniaxial experiment because of its highest Poisson ratio value. The test demonstrated that the deformation of the rubber jacket led to a diameter expansion of 1.5 mm. Assuming a similar behavior for clays, this corresponds to a porosity error less than 7%.

2.2.4 Suspension Experiment

Sample Preparation: clay powder of kaolinite (KGa-1b), a non-swelling clay, was used in the experiments to limit the effects of polar water molecules adsorption (Theng, 1974). To further minimize swelling and the cation exchange capacity, the suspension was prepared in a degassed, 20,000 ppm KCl solution. The size of the K-ion radius, on the order of the kaolinite layer spacing, prevented both cation exchange (Theng, 1974) and water molecules from bounding to any cation in the interlayer position. Measured amounts of clay were added to the water to allow computations of clay content and water saturation. To avoid clumps in the suspension, the powder was sieved before adding it to the water. Trapped air was minimized by constant stirring, shaking, and by using vacuum to de-air the suspension. Acoustic measurements were performed while increasing clay content in the suspension from 0 to 60% using a step of 2% for clay contents less than 40%, and a step of 5% for clay content above 40%. Measurements were discontinued for

clay concentrations greater than 60%: the sample was too viscous to permit a complete outgassing and velocity estimates would be biased by gas content.

Acoustic Measurements: the experimental setup consisted of a Plexiglas container that held the kaolinite – water suspension. Sealed holes on two sides of the container positioned the immersion transducers (1 MHz Panametrics Transducers V303-SU) in the kaolinite – water suspension. In order to avoid reflections from the container sides, the distance between immersion transducers (2.54 cm) was kept shorter than the dimensions of the Plexiglas container (Figure 2). The distance between transducers was fixed during the measurements and was used for velocity computation. The transducers were excited by using a Panametrics (5052 PR) pulser. The signals through the suspension were received and digitized by a digital Tektronix oscilloscope (TDS 420 A) and stored on a computer. At each clay concentration two signal acquisitions were taken to ensure the repeatability of measurements. P-wave quality factor (Q_p) was calculated from the stored signal waveforms by the spectral ratio technique (Toksöz et al, 1979; Prasad & Manghnani, 1997). The signal from the initial KCl water solution was recorded and used as reference signal. In this way similar conditions were maintained for the reference and the sample.

3 RESULTS

3.1 Grain Density, Porosity, and Sample State,

Table 1 compares grain- and bulk- density, and porosity values measured using the methods described in Section 2.2.1.

Differences in grain densities values for most of samples were less than 2% except for Na- montmorillonite samples ($\approx 7\%$). Swelling of this clay mineral, which affects volume

estimate, was noted during the measurement. For Na-montmorillonite samples we will refer to physical properties measured by the He-porosimeter.

Table 1 also shows that clay mineralogy controls both porosity and state of samples obtained by the cold-pressing procedure described in Section 2.2.2. Upon removal of samples from the cold-pressing apparatus, well-compacted low porosity ($4 < \Phi < 20$) samples of Na-, Ca-montmorillonite (Na-Mt, Ca-Mt), and smectite (Sm) were obtained (Figure 3a). On the contrary, illite (Imt) and chlorite (Ch) samples presented higher porosity ($20 < \Phi < 30$) and slowly deteriorated with microcracks forming perpendicular to the applied stress direction (for example, sample Ch in Figure 3b). This effect was most pronounced in kaolinite samples, which completely disaggregated on removal from housing apparatus (sample Ka1 in Figure 3b). Since deterioration of samples was typical of clays without water interlayers, and it occurred both at room humidity and under vacuum (samples Ka1 and Ch), this behavior could be related to clay mineralogy. This hypothesis was confirmed by cold-pressing two dehydrated powders from the smectite group which, in their natural hydrated state, produced good samples (Figure 3a). Figure 3b shows that the dehydrated Sm and Ca-Mt samples disaggregated upon the removal of the cold-pressing pressure. The results from the cold-pressing experiment show that water interlayers in the clay mineral structure play an important role in the compaction and strength of clay aggregates.

3.2 Acoustic Measurements on Cold-Pressed Samples under hydrostatic pressure

Because of their lowest porosity, samples of smectite and Na-montmorillonite were used for the hydrostatic pressure experiment. The experiment was repeated on different samples to ensure repeatability of measurements. In Figure 4 and Figure 5, measurements

of velocity and elastic moduli are reported for the smectite sample as functions of pressure and porosity, respectively. Because of the initial low porosity of smectite sample (4.5%), it was possible to measure velocities and elastic moduli at porosities as low as 0.8% at confining pressure of 20 MPa. Extrapolation using polynomial fit to the data (Table 2) show that, at 0% porosity, $V_p = 2.3$ km/s, $V_s = 1.3$ km/s, $K = 6$ GPa, and $\mu = 4$ GPa. Figure 4 shows that velocity values measured during un-loading are higher than those measured during increasing pressure. Although the sample is allowed to re-equilibrate after pressure release, porosity is not readily recovered in clay and, as consequence, velocity is higher. As pressure decreases, this effect is less evident since the sample has had enough time to re-equilibrate; below 5 MPa the time-lag in recovering of porosity is less pronounced.

3.3 Acoustic Measurements in Uniaxial Stress Condition

In this experiment we monitored velocity and elastic moduli variations during uniaxial stress compaction of kaolinite and Na-montmorillonite powders. Figure 6 shows the variations in velocity and elastic moduli as functions of porosity for kaolinite (Ka1) and montmorillonite (Na-Mt) in dry condition. At the lowest porosity, a linear fit to the data gives elastic moduli for kaolinite mineral as 11 GPa for K and 6 GPa for μ , respectively. Measurements on Na-montmorillonite provided moduli of 11GPa for K and 5.5 GPa for μ (Table 2). The different trends shown in the hydrostatic and uniaxial stress compaction experiments could depend on the dissimilar aggregation state of the used samples. In the uniaxial experiment, we capture the entire compaction curve from the clay powder, having negligible pore stiffness, to very low porosity aggregate. Whereas in the hydrostatic case, since we have pre-compressed the Sm sample, we are looking at the

lower-most porosity of the compaction curve. Future measurements will show whether and how the velocity – porosity trend deviates from a linear trend at very low porosity.

3.4 Acoustic Measurements in Kaolinite-Water Suspension

Figure 7 shows the variation of bulk modulus (Fig. 7a) and quality factor (Fig. 7b) as functions of clay content in the suspension. Bulk modulus was calculated from V_p and density measurements by assuming $\mu=0$, that is, shear wave did not propagate through the suspension. In Figure 7a, at clay concentrations below 40%, bulk modulus (K) increases slightly with increasing clay content. Beyond 40% there is a change in the slope of the bulk modulus increase. In Figure 7b, the P-wave quality factor (Q_p) decreases with increasing clay content and reaches a minimum at 40% clay concentration. After this minimum, Q_p increases with increasing clay concentration.

The behavior of K as a function of increasing clay content is similar to the results of V_p in clay – sand mixtures reported by Marion *et al.* (1992). Marion *et al.* (1992) show that when clay volume fraction (C) is less than 0.4-0.45 (as in Fig.7a), clay particles are suspended in the pore space of the load-bearing medium (sand in their case, water in this study) and velocity measurements reflect mainly a density effect. Q_p decreases due to scattering at possible clumping of the clay. At clay volume fractions greater than 0.4-0.45, clay becomes the load-bearing phase and water (or sand) becomes dispersed in the pore space of the load-bearing clay. Above this point, the increased stiffness due to the clay overweighs density and scattering effects and both K and Q_p increase with increasing clay content. Note that although degassing under vacuum was problematic above 40% clay content, we do not expect a significant quantity of gas bubbles to be present. Presence of gas in the suspension would lower V_p and it would lower Q_p .

significantly. The increase in Qp at clay concentrations larger than 40% (Fig. 7b) suggests that gas concentrations might have been negligible.

4 VELOCITY MODELING

Both our experiments on cold-pressed samples gave consistent values of bulk modulus in the range 6-11 GPa and shear modulus 4-6 GPa that agree with the measurements of Prasad *et al.* (2002). We first compare our results with those reported by Katahara (1986), Wang *et al.* (2001) and Prasad *et al.* (2002) by using them as input in the Hashin-Shtrikman model (Hashin *et al.*, 1963) and the modified Voigt average (Nur *et al.*, 1991; 1998) to calculate bulk modulus of a kaolinite-water suspension. K_{water} was taken as 2.2 GPa (Mavko *et al.*, 1998). Note that in a homogeneous fluid suspension, where $\mu = 0$, the Hashin-Shtrikman lower bound is equivalent to the isostress Reuss average (K_{reuss}) of the composite given by

$$\frac{1}{K_{\text{reuss}}} = \sum_{i=1}^N \frac{f_i}{K_i}, \quad (1)$$

where N is the number of components and f_i is the fraction of the component.

In Figure 8, Hashin-Shtrikman upper and lower bounds of the bulk modulus (Hashin *et al.*, 1963) and the modified Voigt average (Nur *et al.*, 1991; 1998) of a water-clay mixture are compared to experimental measurements in saturated kaolinite samples (Yin, 1993) and in kaolinite–water suspensions (this study). In Figure 8a, the calculations were made using $K = 12$ GPa and $m = 6$ GPa for bulk and shear modulus of the solid phase, respectively (Prasad *et al.*, 2002; this study). Calculations with $K_s = 56$ and $\mu_s = 32$ GPa (Katahara, 1986) and $K_s = 47.9$ and $\mu_s = 19.7$ GPa (Wang *et al.*, 2001) are shown in 8b. In

Figure 8a, the lower HS bound lies on the values measured in the kaolinite–water suspensions and the Modified Voigt Average (MVA) predictions agree with measurements in the saturated kaolinite sample from Yin (1993). These predictions support the conceptual first-principles based model of Dvorkin *et al.* (1999) and Prasad and Dvorkin (2000) wherein the softer material (water) is load-bearing above critical porosity (Φ_c) (Nur et al., 1998) and the system is adequately described by the lower HS bound. Once the stiffer material (clay) becomes load-bearing, as in the saturated kaolinite sample, the measured velocity values move away from the lower HS bound and are better predicted by the Modified Voigt Average (MVA). As described in Nur et al., (1998), critical porosity separates the domain in which a rock sample is frame-supported ($\Phi_{\text{sample}} < \Phi_c$) from that in which it is fluid-supported ($\Phi_{\text{sample}} > \Phi_c$).

The higher values of bulk and shear moduli ($K_s=56$ and $\mu_s=32$ GPa; $K_s=47.9$ and $\mu_s=19.7$ GPa) from Katahara (1986) and Wang *et al.* (2001) respectively, overpredict experimental measurements both for kaolinite-water suspensions and for kaolinite samples (Figure 8b).

As second test, we calculated Vp in shaley sandstones using the different K_s and μ_s values as above for clay and $K_s= 36.6$ GPa and $\mu_s= 45$ GPa for quartz (Mavko *et al.*, 1998). Han *et al.* (1986) have shown that velocity in sandstones is dependent on porosity and on clay content: at the same porosity, clay rich sandstones have lower velocity than clean sandstones. Theoretical velocities calculated with the rock physics model reported in Dvorkin *et al.* (1999) and Prasad and Dvorkin (2001) are compared to velocities measured on clean and clay-rich sandstones at 40 MPa confining pressure (Tosaya, 1982; Han *et al.*, 1986; Klimentos, 1991) in Figure 9. This model uses the Hertz-Mindlin

(Mindlin, 1949) contact theory to first compute the effective bulk (K_{HM}) and shear (μ_{HM}) moduli of a dry mixture of quartz and clay at critical porosity (Φ_c) (Nur et al., 1998) under a given pressure. Next, the upper and lower Hashin-Shtrikman bounds (1963) are calculated between the two end- points at zero porosity (K_s , μ_s) and at the critical porosity (K_{HM} , μ_{HM}) for this two-component mixture of quartz and clay. Finally, the elastic moduli of water-saturated clay-quartz mixture are calculated using Gasmann's fluid substitution equations (see Dvorkin *et al.*, 1999 and Prasad and Dvorkin, 2001 for details). As in Figure 8, Figure 9a shows theoretical curves for the clay mineral moduli, $K_s = 12$ GPa and $\mu_s = 6$ GPa and Figure 9b for $K_s = 47.9$ GPa and $\mu_s = 19.7$ GPa. Figures 9a and 9b, show theoretical curves computed for clay contents values of 5%, 15%, 25%, and 50%. The computations show that in a two phase system, if the individual phases have similar elastic moduli, then increasing the concentration of one phase over the other will not alter the moduli of the composite system. Thus, in Figure 9b, since the moduli of clay ($K_s = 47.9$ GPa and $\mu_s = 19.7$ GPa) and quartz ($K_s = 36.6$ GPa and $\mu_s = 45$ GPa) are very similar, the model does not predict a significant modulus reduction with increasing clay content. Using the moduli obtained from this study and from Prasad et al. (2002), we get a much better agreement between model prediction and experimental data (Figure 9a) Figure 9a shows that lower moduli of clay explain both the reduction of the velocity as a function of clay content and the separation in measured velocities due to addition of clay to the sandstones.

5 CONCLUSIONS

We have measured elastic moduli values between 6 and 12 GPa for bulk (K_s) and between 4 and 6 GPa for shear (μ_s) in kaolinite, montmorillonite, and smectite clay

minerals. These results, obtained using different sample preparation and measurements techniques are consistent with one other and those obtained with Atomic Force Acoustic Microscopy by Prasad et al. (2002). They are also comparable to values extrapolated and modeled from laboratory and log measurements on shales (Han, 1986; Castagna et al., 1985; Berge and Berryman, 1995).

Note that our measurements are much lower than the theoretical extrapolations of Katahara (1996) and measurements on clay-epoxy mixtures (Wang et al., 2001). We suggest that a possible reaction between clay minerals and the polar organic epoxy fluid might lead to a super-dry clay with a higher mineral modulus.

In addition to the consistency check, we modeled the elastic moduli in binary systems: porous clay-quartz and water-kaolinite. We used values measured in this study and those from Katahara (1996) and Wang et al. (2001) for clay mineral moduli. Using $K_s=12$ GPa and $\mu_s=6$ GPa from this study, the model gives a much better prediction both of experimental velocity reduction due to increase in clay content in sandstones and velocity measurements in a kaolinite water suspension.

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REFERENCES

- Alexandrov, K. S., and T.V. Ryzhova, 1961. Elastic properties of rock-forming minerals II layered silicates, *Bull. U.S.S.R. Acad. Sci., Geophys. Ser.*, **9**, 1165-1168.
- ASTM, 1992. Standard specifications for grain density determination of soils, *ASTM Designation D854-92*, American Society for Testing Materials.

- Berge, P. A., and J. G., Berryman, 1995. Realizability of negative pore compressibility in poroelastic composites, *Journal of Applied Mechanics*, **62**, 1053-1062.
- Brace, W.F., Scholtz, C.H., and La Mori, P.N., 1969. Isothermal compressibility of kyanite, andalusite, and sillimanite from synthetic aggregates, *J. geophys. Res.*, **74**, 2089-2098.
- Castagna, J. P., Han, De-hua, and Batzle, M. L., 1985. Issues in rock physics and implications for DHI interpretation, *The Leading Edge*, 883-885.
- Chung, D.H., 1979. Elasticity of Stishovite revisited: in *High pressure science and technology*, K.D. Timmerhaus and M.S. Baber, Plenum Publishing Corp.
- Colten Bradley, V. A., 1987. Role of pressure in smectite dehydration-effects on geopressure and smectite-to illite transformation, *AAPG Bulletin*, **71**, 11, 1414-1427.
- Dvorkin, J., Prasad, M., Sakai, A., Lavoie, D., 1999. Elasticity of marine sediments: Rock Physics Modeling: *Geoph. Res. Lett.*, **26**, 12, 1781-1784.
- Eastwood, R. L., and Castagna, J. P. 1987. Interpretation of Vp/Vs ratios from sonic logs, *Geophysical Developments*, **1**, 139-153.
- Han, De-hua, 1986. *Effects of porosity and clay content on acoustic properties of sandstones and unconsolidated sediments*, Ph.D. Dissertation, Stanford University, Stanford.
- Han, De-hua, Nur, A., and Morgan F. D., 1986. The events of porosity and clay content on wave velocities in sandstones, *Geophysics*, **51**, 2093-2107.
- Hashin, Z., and Shtrikman, S., 1963. A variational approach to the elastic behavior of multiphase materials, *J. Mech. Phys. Solids*, **11**, 127-140.
- Katahara, K. W., 1996. Clay mineral elastic properties, *SEG Annual Meeting Expanded Technical Program Abstracts*, Paper RP1.4,
- Klimentos, T., 1991. The effects of porosity-permeability-clay content on the velocity of compressional waves, *Geophysics*, **56**, 12, 1930-1939.
- Koster Van Groos, A.F., and S. Guggenheim, 1984. The effect of pressure on the dehydration reaction of interlayer water in Na-montmorillonite (SWy-1), *American Mineralogist*, **69**, 9-10, 872-879.
- Kowallis, B. J., Jones, L. E. A., and Wang, H. F., 1984. Velocity-porosity-clay content systematics of poorly consolidated sand-stones, *J. geophys.. Res.*, **89**, 10355-10364.
- Marion D., Nur A., Yin H., and Han D., 1992. Compressional velocity and porosity in sand-clay mixtures, *Geophysics*. **57**, 554-363.
- Mavko, G., T. Mukerjy, and J. Dvorkin, *Rock Physics Handbook*, Cambridge University Press, 1998.
- Mindlin, R. D., 1949, Compliance of elastic bodies in contact: *Trans. ASME*, **71**, A-259.
- Newman A. C. D., 1987. *Chemistry of clays and clay minerals*, vol.6, pp. 480, Mineralogical Society, London, United Kingdom.
- Nur, A., Marion, D., and Yin, H., 1991. Wave velocities in sediments, in *Shear Waves in Marine Sediments*, J. M. Hovem et al., eds. Kluwer Academic Publishers, Dordrecht, The Netherlands, 131-140.
- Nur, A., Mavko, G., Dvorkin, J., and Galmudi, D., 1998. Critical porosity: A key to relating physical properties to porosity in rocks, *The Leading Edge*, **17**, 3, 357-362.
- Prasad, M., and M.H. Manghnani, 1997. Effects of pore and differential pressures on compressional wave velocity and quality factor on Berea and Michigan sandstones: *Geophysics*, **62**, 4, 1163-1176.

- Prasad, M., Dvorkin, J., 2001. Velocity to porosity transforms in marine sediments, *Petrophysics*, **42**, 5, 429 - 437.
- Prasad, M., Kopycinska, M., Rabe, U., and Arnold, W., 2002, Measurement of Young's modulus of clay minerals using Atomic Force Acoustic Microscopy, *Geoph. Res. Lett.*, **29**, 8.
- Theng, B. K. G., 1974. *The chemistry of clay-organic reactions*, pp. 343, Adam Hilger Ltd Ed., London, United Kingdom.
- Toksöz, M. N., Johnston, D. H., and Timur, A., 1979. Attenuation of seismic waves in dry and saturated rocks, I. Laboratory measurements, *Geophysics*, **44**, 681-690
- Tosaya, C. A., 1982. *Acoustical properties of clay bearing rocks*, Ph.D. Dissertation, Stanford University, Stanford.
- Tosaya, C. A., and Nur, 1982. A., Effect of diagenesis and clays on compressional velocities in rocks, *Geophys. Res. Lett.*, **9**, 5-8.
- Vanorio, T., Prasad, M., Patella, D., and Nur, A., 2002, Ultrasonic velocity measurements in volcanic rocks: correlation with microtexture, *Geoph. J. Int.*, **149**, 22-36.
- Vernik, L., and X Liu, 1997, Velocity anisotropy in shales: A petrophysical study, *Geophysics*, **62**, 2, 521-532.
- Wang, Z., H. Wang, and M.E. Cates, 2001. Effective elastic properties of solid clays, *Geophysics*, **66**, 2, 428-440.
- Yin H., 1993. *Acoustic velocity and attenuations of rocks: isotropy, intrinsic anisotropy, and stress induced anisotropy*, Ph.D. Dissertation, Stanford University, Stanford.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1. Porosity, bulk- and grain- density of cold-pressed clay samples

Pycnometer			He-Porosimeter			Pycnometer			He-Porosimeter				
Sample	Rhog g/cm ³	Φ %	Rhob g/cm ³	Rhog g/cm ³	Φ %	Rhob g/cm ³	Sample	Rhog g/cm ³	Φ %	Rhob g/cm ³	Rhog g/cm ³	Φ %	Rhob g/cm ³
Ka1	2.59	43	1.48	Nm ^a	Nm	Nm	Sm3	2.29	6	2.15	2.28	6	2.15
Ka2	2.59	43	1.48	Nm	Nm	Nm	Sm4	2.29	4	2.19	2.30	5	2.19
Na-Mt1	2.30	13	2.00	2.47	11	2.19	Sm5	2.29	22	1.80	2.30	22	1.80
Na-Mt2	2.30	9	2.09	2.44	10	2.19	Sm6	2.29	10	2.05	2.29	10	2.05
Na-Mt3	2.30	14	1.99	2.47	20	1.99	Ca-Mt-1	2.13	22	1.68	2.14	22	1.68
Na-Mt4	2.30	12	2.02	2.48	18	2.02	Ca-Mt-2	2.13	21	1.69	2.13	21	1.69
Na-Mt5	2.30	11	2.05	2.47	17	2.05	Ca-Mt-3	2.13	17	1.76	2.13	17	1.76
Na-Mt6	2.30	19	1.85	2.47	25	1.85	Ca-Mt-4	2.13	21	1.67	2.12	21	1.67
Sm1	2.29	8	2.11	2.29	7	2.13	CH3	2.83	25	2.03	Nm	Nm	Nm
Sm2	2.29	13	1.99	2.29	13	1.99	Imt1	2.68	22	2.10	Nm	Nm	Nm

^a Not-measurable samples

Table 2. Values of polynomial curves fit to the data

Smectite $M=a\Phi^4+b\Phi^3+c\Phi^2+d\Phi+e$						
M	a	b	c	d	e	R ²
Vp	0.011	-0.138	0.613	-1.184	2.321	(0.98)
Vs	0.005	-0.054	0.242	-0.471	1.324	(0.98)
K	0.026	-0.310	1.355	-2.603	5.75	(0.98)
μ	0.049	-0.601	2.682	-5.212	4.02	(0.99)
Kaolinite and Na-Montmorillonite $M=a\Phi+b$						
M	a	b	R ²	a	b	R ²
Vp	-0.03	2.695	(0.97)	-0.05	2.748	(0.97)
Vs	-0.01	1.436	(0.95)	-0.02	1.496	(0.96)
K	-0.21	11	(0.97)	-0.35	11	(0.99)
μ	-0.10	6	(0.96)	-0.15	5.5	(0.99)

BIBLIOGRAPHY

Vanorio, T., Prasad, M., and Nur, A.: Elastic Properties of Dry Clay Mineral Aggregates, Suspensions and Sandstones, to appear in *Geophysical Journal International*.