Rock-physics templates for hydrocarbon source rocks Short title: Rock-physics templates for source rocks

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Contents

1	Introduction
2	Kerogen/oil/gas and smectite/illite conversions
3	Effective-media models
4	Model calibration
5	Rock-physics templates 13
6	Conclusions
Α	Oil/gas generation and shale diagenesis
В	Properties of hydrocarbon gas
\mathbf{C}	Properties of oil and brine
D	Effective fluid model for partial gas saturation
Е	Properties of the kerogen/fluid mixture
\mathbf{F}	Dry-rock elasticity constants
\mathbf{G}	Petro-elastical models
Η	Energy velocity and wavefront
Ι	AVO classes of a source-rock layer 32
J	List of symbols
Κ	Tables 34
L	Figures

Abstract Shale source rocks are complex systems whose frame is composed of various minerals, mainly smectite and illite, depending on the burial depth. The "pore space" may contain kerogen, water, oil and gas determined by the in-situ conditions of temperature and pressure. From the rheological point of view, source rocks can be described as transversely isotropic media. To obtain a petro-elastical description of shales with

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these characteristics, we follow several steps. Smectite to illite transformation is taken into account as a function of depth by means of a 5th-order kinetic reaction. Backus averaging to "mix" isotropic smectite and anisotropic illite is then used to obtain the elasticity constants of the mineral composing the shale frame. Porosity is obtained from densities, and water is assumed to saturate the composite mineral, whose elasticity constants are obtained from Gassmann equations based on an anisotropic frame. Oil and gas generated from kerogen are assumed to saturate the kerogen phase. The bulk modulus of the oil-gas mixture is calculated by using a mesoscopic-loss model of patchy saturation, and the bulk and shear moduli of the kerogen/fluid mixture are obtained with the Kuster and Toksöz model, assuming that the fluid is the inclusion in a kerogen matrix. Two different models are considered to obtain the seismic velocities of the shale, namely, Backus averaging and Gassmann equation generalized to the anisotropic case with a solid pore infill. The latter model requires the dry-rock or frame elasticity constants, which are obtained with a generalization of Krief equations to the anisotropic case or the inverse Gassmann equation if data is available.

We build different types of rock-physics templates for shales containing only kerogen (immature) and kerogen plus hydrocarbons (mature). Pore pressure effects are also taken into account and shown as templates. We consider an specify example where the Kimmerigde shale (Spekk formation) appears at different depths. To model kerogen-oil and oil-gas conversions, starting at depths determined by temperature, we assume a simple basin-evolution model with constant sedimentation rate and geothermal gradient and a first-order kinetic reaction, with a reaction rate satisfying the Arrhenius equation. In particular, the possibility of detecting the presence of the hydrocarbons is investigated from rock physics templates built with wave velocities, impedances, Lamé constants, density, Poisson ratio, Young modulus and anisotropy parameters for varying kerogen content, fluid saturations and pore pressure. Moreover, AVO intercept and gradients are computed, corresponding to the seismic response of a source rock layer for varying kerogen content and fluid saturation.

Keywords source rock, kerogen, oil, gas, Backus, Gassmann, smectite/illite, AVO, rock-physics templates

1 Introduction

Rock-physics templates (RPT) establish a link between the elastic properties (e.g., velocity, density, impedance, wet-rock stiffness moduli) and the reservoir properties such as porosity, fluid saturation and clay content in sandstones or kerogen content and hydrocarbon saturation in source rocks. Specific examples can be found in Ødegaard and Avseth (2004), Avseth et al. (2005) and Chi and Han (2009). Building a template requires calibration with well-log data. There are several steps to calibrate and use the templates: i) Obtain the effective properties of the grain minerals and pore-infill material; ii) Determine the properties of the dry rock; iii) Obtain the wet-rock velocities and mass density with a suitable model (Backus averaging and Gassmann equation are used here); iv) Perform pore-infill substitution to determine the location of each specific pore-infill component in the RPT; v) Report the seismic properties on the templates to create TOC (total organic content) and fluid saturation maps of the studied area.

In the case of source rocks the analysis with RPT is scarse. Zhu et al. (2012) use the Gassmann-type model developed by Carcione et al. (2011) to incorporate TOC effects, mineralogy, porosity, and fluid content, and describe the seismic properties of shale gas. Their modeling indicates that an increase in TOC generally reduces the P-wave impedance and the v_P/v_S ratio, increasing the velocity anisotropy, as already shown by Carcione (2000), where v_P and v_S denote the P- and S-wave velocities. Cerón et al. (2013) analyse a number of shale cores of the Cretaceous Colombian basin showing the presence of organic content. Density cross-plots and permeability-porosity templates are shown. Yenugu and Han (2013) use Carcione's approach (Carcione, 2000) to model the degree of maturity of the shale and obtain its elastic properties and related AVO effects. Bakken shale has class IV AVO and its amplitude is affected by kerogen maturity.

Oil and gas can be generated in kerogen rich shales at the oil and gas windows, where the amount of conversion depends on temperature. Carcione (2000) and Pinna et al. (2011) have quantified the conversion as a function of the sedimentation rate and geothermal gradient using the Arrhenius equation. The model assumes one reaction rate and a closed system; here we assume that the kerogen to gas conversion is negligible (gas is generated from oil). As Pepper and Corvi (1995) state: "gas yields directly from kerogen are not the prime causes of gas-proneness in source rocks". On the other hand, the conversion from smectite to illite (clay diagenesis) with increasing depth occurs in all shales (Scotchman, 1987) and can be described by the widely accepted model proposed by Pytte and Reynolds (1989) based on a 5th-order kinetic reaction of the Arrhenius type. The result of the conversion is that the stiffnesses of the mineral composing the shale increase with depth. Backus averaging is then used to obtain the properties of the smectite-illite mixture.

Research conducted by Vernik on petroleum source rocks (Vernik and Nur, 1992; Vernik, 1994, 1995; Vernik and Landis, 1996) indicates that strong velocity anisotropy is associated with the presence of organic matter and the layered nature of the single components. Vernik (1995) and Carcione (2000) use Backus averaging to describe the elastic properties. Carcione et al. (2011) have used Ciz-Shapiro (Gassmann) equation for an anisotropic frame and an isotropic solid pore infill (kerogen-oil) (Ciz and Shapiro, 2007). The dry-rock elasticity constants involved in Gassmann equation are obtained by a generalization of Krief equations to the anisotropic case (see the isotropic version in Krief et al. (1990)). In this case, by "dry rock" we mean the rock excluding the pore-fill (kerogen, water oil and gas), while "wet rock" refers to the rock including the pore-fill. Bound water is part of the rock frame. Figure 1 shows a scheme where porosity is defined according to the elastic model used. The effect of partial saturation on velocity depends on the location of the so-called mesoscopic-loss peak in the frequency axis (e.g., Carcione, 2007; Carcione and Picotti, 2006). When oil and gas are generated in a kerogen matrix, the gas bubbles embedded in oil cause a wave-induced fluidflow attenuation mechanism which yields velocity dispersion. The location of the peak depend mainly on the size of the gas pockets, and the bulk modulus of the fluid mixture differs from Wood (or Reuss) modulus. The model used to compute the modulus is based on White theory (e.g., Carcione, 2007). On the other hand, the PP reflection coefficients of a source-rock layer as a function of the layer thickness and organic content has been obtained by Carcione (2001b). Here we analyse the AVO class of a thin sourcerock layer from AVO crossplotting based on Shuey's two-term approximation. Details of the algorithms to compute the scattering coefficients can be found in Carcione (2001a,b)

2 Kerogen/oil/gas and smectite/illite conversions

To obtain the fraction of oil and gas at a given depth, we assume: i) no loss of fluid from the source-rock pore volume (a closed system with negligible permeability); ii) the initial pore volume contains only convertible kerogen, since water content is relatively small and is part of the matrix (smectite/illite); iii) Kerogen/oil and oil/gas conversion are two independent processes (Berg and Gangi, 1999). The model is given in Appendix

5

A and consider two separate kinetic reactions describing the kerogen/oil and oil/gas conversions.

Moreover, it is important to evaluate the amount of smectite/illite ratio forming the shale matrix, since this ratio affects the stiffness moduli and wave velocities of the rock. Shale mineralogy may include kaolinite, montmorillonite-smectite, illite and chlorite, so the term smectite-illite as used in this study may be representative for a mixture of clay minerals (Mondol et al., 2008). In the Kimmeridge clay there is also some percentage of silty quartz (Williams et al., 2001). Moreover, the smectite-illite layers represent an assembly of platelets, subject to internal hydration, so its mechanical properties such as the stiffnesses can vary depending on the source rock.

The conversion smectite/illite occurs in all shales with a general release of bound water into the pore space (Scotchman, 1987). Smectite dehydration implies a stiffer matrix due to the presence of more illite and therefore higher velocities. The conversion depends on temperature and sedimentation rate. A solution to this problem has been provided by Pytte and Reynolds (1989) (see Appendix A). Smectite and illite are then "mixed" by using Backus averaging (66) to obtain the elasticity constants of the mineral composing the frame.

3 Effective-media models

We consider two models to obtain the stiffness moduli and wave velocities of the source rock, namely Backus averaging (Schoenberg and Muir, 1989; Vernik, 1994; Carcione, 2000, Carcione et al., 2011, Pinna et al., 2011) and Gassmann equation for a solid pore infill (Ciz and Shapiro, 2007; Carcione et al., 2011). The rock geometry corresponding to these models is shown schematically in Figure 2, where a) depicts the model used by Backus to represent a system of plane layers whose thicknesses are much smaller compared to the wavelength of the signal, b) shows a modification of Backus model taking into account the discontinuity of the illite layers in the shale fabric, and (c) is a representation of the shale based on Gassmann's assumptions to represent a porous medium. Regarding model b), SEM observations have shown that the illite fabric has a lenticular pattern along the bedding plane rather a continuous-layer structure (Vernik and Nur, 1992). A reasonable way to model this effect is to substitute the bedding-plane elastic stiffnesses by a weighted average that takes into account the local proportion of illite and kerogen. In the Gassmann model, the liquid phase is continuous and the pore space can have any shape as shown in Figure 2c.

We report in the appendices the equations to obtain the fluid properties (B, C and D). We assume that the kerogen-oil-gas mixture consists of oil-gas bubbles embedded in a kerogen matrix (Appendix E). Calculation of the Gassmann moduli requires to know the dry-rock elasticity constants. These are obtained by a simple generalization of the Krief model (Krief at al., 1990) (see Appendix F). Backus averaging and Gassmann equations are given in some detail in Appendix G. The quantities K, μ , and ρ indicate bulk modulus, shear modulus and density, respectively, v_P and v_S denote P-wave and S-wave velocities, and the indices m, s, w, o, g, f, k and if denote dry matrix (frame or skeleton), solid grain (clay minerals), water (brine), oil, gas, fluid (oil-gas mixture), kerogen and pore infill (oil-gas-kerogen mixture), respectively. Moreover, c_{IJ} denotes the two-index notation for stiffnesses (Helbig, 1994) and ϕ denotes porosity or proportion of a given material.

The quantities to build the templates are given in the following. The compressionalwave and shear-wave impedances

$$I_P = \rho v_P^2, \quad I_S = \rho v_S^2, \tag{1}$$

respectively, the Lamé constants

$$\lambda = \rho(v_P^2 - 2v_S^2), \quad \mu = \rho v_S^2;$$
(2)

three dynamic Poisson's ratios, corresponding to different directions

$$\nu_1 = \frac{\bar{c}_{12}\bar{c}_{33} - \bar{c}_{13}^2}{\bar{c}_{11}\bar{c}_{33} - \bar{c}_{13}^2}, \quad \nu_2 = \frac{\bar{c}_{13}(\bar{c}_{11} - \bar{c}_{12})}{\bar{c}_{11}\bar{c}_{33} - \bar{c}_{13}^2}, \quad \nu_3 = \frac{\bar{c}_{13}}{\bar{c}_{11} + \bar{c}_{12}} \tag{3}$$

(Carcione and Cavallini, 2002); the anisotropy parameters

$$\epsilon = \frac{\bar{c}_{11} - \bar{c}_{33}}{2\bar{c}_{33}}, \quad \gamma = \frac{c_{\bar{6}6} - \bar{c}_{55}}{2\bar{c}_{55}}, \quad \delta = \frac{(\bar{c}_{13} + \bar{c}_{55})^2 - (\bar{c}_{33} - \bar{c}_{55})^2}{2\bar{c}_{33}(\bar{c}_{33} - \bar{c}_{55})} \tag{4}$$

(Thomsen, 1986); and the Young modulus, defined as

$$Y = 2\bar{c}_{55}(1+\nu_i), \quad i = 1, 2, 3.$$
(5)

See Appendix I to obtain the AVO intercept and gradient and identify the AVO classes of a source-rock layer.

4 Model calibration

We consider the Spekk formation (a Kimmerigde shale in the North Sea). This formation is an Upper Jurassic to Lower Cretaceous black shale located on the mid-Norwegian shelf (Langrock, 2004). We have wireline logs from three wells, with average depths of 1.7, 2.4 and 2.6 km (wells 1, 2 and 3, respectively). Wells 1 and 3 are used for the calibration. First, we quantify the oil and gas saturations as a function of depth due to kerogen and oil conversions, respectively. As Berg and Gangi (1999), we consider a single activation energy. The "J70 Upper Jurassic Kimmeridge Clay Formation" is indicated as organofacies B in Pepper and Corvi (1995). The geothermal gradient in the studied area is G = 37 °C/km (well reports), the sedimentation rate is S = 0.04 mm/y (Ebukanson and Kinghorn, 1990) and the surface temperature is 15 $^{\circ}$ C. The assumed activation energies are E = 28000 cal/mol (kerogen/oil) and E = 30000 cal/mol (oil/gas), while the infinite-temperature rate is $A = 10^{13}$ /m.y. for oil and gas. Values of these parameters can be found in Pepper and Corvi (1995) and Berg and Gangi (1999) for instance. Figure 3a shows the fraction of kerogen converted to oil and the fraction of oil converted to gas. With these values of the kinetic parameters, the shale in well 1 has kerogen, while the shale in well 3 is partially saturated with oil. Assuming the properties of kerogen, oil and water shown in Table 1 (at 3 km) and S_w = 10 %, Figure 3b displays the pore pressure generated due to the kerogen/oil conversion $(\phi' = 0.3 \text{ in equation (22) is assumed})$. The hydrostatic and lithostatic pressures are obtained as $p_H = \bar{\rho}_w gz$ and $p_c = \bar{\rho} gz$, respectively, where $\bar{\rho}_w = 1.04 \text{ g/cm}^3$, $\bar{\rho} = 2.4$ g/cm^3 , z is depth and $g = 9.81 m/s^2$. Since oil cannot escape from the pore space (zero permeability), the pore pressure rapidly reaches the lithostatic pressure where failure occurs. This happens at 3.3 km depth where 10 % of the kerogen has been converted to oil. However, this is uncertain due to the lack of data. Regarding the following model calibration, we assume that the shale is fully saturated with kerogen at wells 1 and 3.

The kinetic reaction corresponding to smectite/illite conversion assumes E = 39000 cal/mol and $A = 1.217 \times 10^{23}$ / m.y. (Pytte and Reynolds, 1989). We consider that at 1.8 km depth the smectite/illite ratio is $r_0 = 0.99$. The kinetic-reaction parameters have been obtained by matching the log bulk density with the theoretical expression of the bulk density (see Figure 7b below). The conversion ratio is shown in Figure 4. As can be seen, smectite and illite are the main components at wells 1 and 3, respectively. The elastic properties of smectite and illite are given in Table 1 (Carcione, 2000; Totten et al., 2002; Carcione et al., 2011; Pinna et al., 2011). Due to compaction effects, we assume that the density of kerogen is 1.2 g/cm^3 at well 1 and 1.3 g/cm^3 at well 3.

The density of illite is an upper limit at very large confining pressures and can also be due the presence of pyrite and carbonates. Smectite is assumed isotropic and its values have been taken from Wang et al. (2001). On the basis of the smectite and illite fractions given in Figure 4, we have computed the P- and S-wave bedding-normal phase velocities and density $\rho_s = \rho_{sm}r + \rho_i(1-r)$ of the mineral composing the frame, where ρ_{sm} and ρ_i are the densities of smectite and illite, respectively (Figure 5).

From well reports, we have precise values of TOC of the Spekk formation at given depths. In the following, we perform comparisons between the well-log data and model calculations at these depths. This first step constitutes the model calibration assuming that no liquid or gaseous hydrocarbons are present in the source rock. The volumetric kerogen content can be calculated in terms of the total organic carbon (TOC, in weight percentage between 0 and 100) from

$$\mathbf{K} = \frac{(\rho - \phi \rho_w) \mathrm{TOC}}{C_k \rho_k (1 - \phi)},\tag{6}$$

where ϕ is the porosity (water fraction in this case), ρ is the density of the source rock, ρ_k and ρ_w are the densities of kerogen and water, respectively, and C_k depends on the maturity level ranging from 0.7 to 0.85 (Vernik and Nur, 1992; Carcione, 2000; Vernik and Milovac, 2011). An alternative, simplified equation is given in Sondergeld et al. (2010, eq. 12).

On the other hand, the bulk porosity in the absence of hydrocarbons is

$$\rho = \phi \rho_w + \phi_k \rho_k + (1 - \phi - \phi_k) \rho_s, \tag{7}$$

where $\phi_k = K/100$. Combining equations (6) and (7), we solve for porosity from

$$A\phi^{2} + B\phi + C = 0,$$

$$A = \rho_{s} - \rho_{w},$$

$$B = \rho + \rho_{w}(1 - a\rho_{k} + a\rho_{s}) - 2\rho_{s},$$

$$C = \rho_{s} + \rho(a\rho_{k} - a\rho_{s} - 1),$$

$$a = \frac{\text{TOC}}{C_{k}\rho_{k}}$$
(8)

and for kerogen content from equation (6). The bulk density ρ is obtained from the density logs. We assume $C_k = 0.75$, $\rho_w = 1.04 \text{ g/cm}^3$ (well 1) and $\rho_w = 1.02 \text{ g/cm}^3$ (well 3) (see Figure 15 below). TOC and K are represented in Figure 6 as a function of depth, where the average values of K are approximately 14 % and 26 % in wells 1 and 3, respectively.

The density of the shale mineral, shown in Figure 5b, and the porosity from equation (8) are used to calculate the bulk density of the shale (7), where the kerogen content values are obtained from equation (6). Figure 7 shows the porosity derived from equation (8) (a) and the bulk density calculated from equation (7) (open circles) compared to the log bulk density (solid line) (b). As can be appreciated, the comparison is satisfactory.

Alternatively, total organic carbon has been expressed as a function of rock density by an empirical relations in Vernik and Landis (1996) and Carcione (2000) as

$$TOC(wt\%) = 67 \frac{\rho_k(\rho_s - \rho)}{\rho(\rho_s - \rho_k)},$$
(9)

where TOC accounts for approximately 67 % of the bulk kerogen. A comparison to the TOC values given in the well reports is shown in Figure 8, showing a relatively good agreement.

Next, we compute the bedding-normal P-wave velocities v_{33} of the shale using Backus averaging (66) and Gassmann equation (69). We assume that water is saturating the mineral material composed of smectite and illite and use Gassmann equation (69) to obtain the elasticity constants of the mineral/water composite medium. In this case, the pore infill is water (its shear modulus is set to a small value in order for the equation to work). The equations to obtain the elasticity constants of this composite medium require the dry-rock elasticity constants, which are obtained from equations (56) with A = 1.5 and B = 4. Likewise, the same parameters are used to obtain the dry-rock elasticity constants required by Gassmann equation to compute the elasticity constants of the shale saturated with kerogen. Figure 9 shows the bedding-normal Pwave velocities as a function of depth. The solid lines and open circles correspond to the sonic-log data and model calculations, respectively. The agreement is very good, with Backus averaging and Gassmann equations giving similar results for well 3. There is S-wave velocity data only in well 3. Figure 10 compares data and model calculations of the bedding-normal S-wave velocity v_{55} . The agreement in the depth range where the TOC values are known is acceptable. The anisotropy parameters (4) are shown in Figure 11, where strong anisotropy can be observed. Parameter δ is negative in all the cases (the P-wave velocity increases away from the vertical if δ is positive and decreases if δ is negative). The Backus model predict more anisotropy than the Gassmann model.

For comparison, we show in Figure 12 the sonic, density and gamma ray logs. Higher velocities in well 2 indicate that the amount of kerogen in this well can be much lower than those of well 3 in the studied range (2.9 to 3.05 km depth). This fact is also reflected in the bulk density and gamma ray logs, with lower and higher values in well 3, respectively. High kerogen content in well 2 can be hypothesised in the range 2.6 to 2.8 km depth, where P-wave velocity and bulk density show low values and the gamma ray have high values. The previous analysis and these results support the fact that at the calibration wells mainly kerogen is present, since the models match the data without including fluids other than water.

Figures 13 and 14 show the fit of the Spekk formation in well 3, where the symbols correspond to the model predictions (Backus averaging). Gassmann equations provide a similar agreement.

5 Rock-physics templates

The properties of the fluids depend on depth, temperature and pore pressure. Using the equations given in Appendices B and C, an hydrostatic pore pressure $p_H = \bar{\rho}_w gz$, where $\bar{\rho}_w = 1.04 \text{ g/cm}^3$, $s_c = 100000 \text{ ppm}$, API gravity = 50 and G = 37 °C/km, we obtain the densities and bulk moduli shown in Figure 15. To build the templates, we assume similar conditions as those given in well 3, where it is more probable the presence of oil and gas. We then consider a depth of 3 km, that the mineral forming the frame of the shale (smectite-illite-water) has 5 % water ($\phi_w = 0.05$) and that the kerogen fraction can reach a maximum value of 30 % ($\phi_k = 0.3$). The kerogen properties are defined by $K_k = 6.6 \text{ GPa}$, $\mu_k = 2.7 \text{ GPa}$ and $\rho_k = 1.4 \text{ g/cm}^3$ (Carcione, 2000; Carcione et al., 2011; Pinna et al., 2011).

We assume the the pore pressure has been released and remains hydrostatic, otherwise the pressure effect on the rock frame has to be considered (this effect is modeled below). Under these conditions, the mineral properties (including water) and the fluid properties are given in Table 1. To obtain the bulk modulus of the oil-gas mixture, we consider the mesoscopic-loss theory developed in Appendix D. This attenuation mechanism affects the seismic velocity depending in the size of the gas patches. Figure 16 shows the bulk modulus as a function of frequency for different values of the gas-pocket radius, r_0 ($\varphi = 0.3$ is assumed). Wood average, which is normally used, is also shown. We consider $r_0 = 1$ cm in the following calculations.

The proportion of the kerogen-oil-gas mixture is $\phi_k + \phi_f = \phi_k + \phi_o + \phi_g$ and the proportion of solid-water is $\phi_s + \phi_w$, where solid stands for the smectite-illite mixture. The porosity is $\phi = \phi_w + \phi_o + \phi_g$ and we have $\phi_s + \phi_w + \phi_k + \phi_o + \phi_g = 1$. Backus averaging "mixes" the kerogen-oil-gas and the solid-water phases with the respective proportion indicated above. We define the oil and gas saturation as $S_o = \phi_o/\phi$ and $S_g = \phi_g/\phi$, respectively, and the kerogen content is $K = 100\phi_k$. In what follows, we fix the amount of organic content, defined by $\phi_{\rm OC} = \phi_k + \phi_o + \phi_g$ and vary the kerogen, oil and gas proportions. It is $\phi_{\rm OC} + \phi_w + \phi_s = 1$. Summarizing, we have the set of relations

$$\begin{aligned}
\phi_{\rm OC} &= \phi_k + \phi_o + \phi_g, \\
\phi &= \phi_w + \phi_o + \phi_g, \\
S_w &= \phi_w / \phi, \\
S_o &= \phi_o / \phi, \\
S_g &= \phi_g / \phi, \\
\phi_{\rm OC} &+ \phi_w + \phi_s = 1, \\
\phi_o &= S_o (\phi_{\rm OC} + \phi_w - \phi_k), \\
\phi_g &= S_q (\phi_{\rm OC} + \phi_w - \phi_k)
\end{aligned}$$
(10)

and all the quantities greater than zero. The correction to the bedding-parallel stiffness constants of the mixture solid-water when using Backus averaging is not applied here, since it is unstable in the presence of fluids (it gives negative stiffness constants). The density of the kerogen-oil-gas mixture is $\rho_{\rm OC} = (\phi_k \rho_k + \phi_o \rho_o + \phi_g \rho_g)/\phi_{\rm OC}$ and the bulk density is $\rho = (1 - \phi_{\rm OC})\bar{\rho}_s + \phi_{\rm OC}\rho_{\rm OC}$, where $\bar{\rho}_s = (\phi_s \rho_s + \phi_w \rho_w)/(\phi_s + \phi_w)$ is the density of the smectite-illite-water mixture.

Figures 17 and 18 show the bedding-normal (a) and bedding-parallel (b) P-wave velocities as a function of gas saturation for various values of the kerogen content and oil saturation. The models are Backus averaging and Gassmann equation, respectively, and the frequency is 50 Hz. Both models behave similarly at full kerogen saturation as we have previously seen, but predict different behaviours in the presence of fluids, mainly the velocities along the bedding plane. The velocities decrease with decreasing kerogen content, but may increase or decrease as a function of oil and gas saturations due to the density effect. Backus averaging predicts very low normal-bedding velocity at K = 0 %, and high bedding parallel velocities, indicating that this model provides lower and upper limits (Carcione et al., 2011).

The energy velocities for a shale with full kerogen content (immature) (a) and a shale saturated with oil and gas (mature) (b) are shown in Figure 19. Depth is 3 km, $\phi_w = 0.05$, the model is Gassmann equation and the frequency is 50 Hz. In the first case, K = 0.3, $S_o = S_g = 0$, $\bar{c}_{11} = 37.3$ GPa, $\bar{c}_{13} = 6.21$ GPa, $\bar{c}_{33} = 22.33$ GPa, \bar{c}_{55} = 7.70 GPa, $\bar{c}_{66} = 14.04$ GPa and $\bar{\rho} = 2347$ kg/m³; in the second case it is K = 0, S_o = 0.7, $S_g = 0.15$, $\bar{c}_{11} = 29$ GPa, $\bar{c}_{13} = 1.64$ GPa, $\bar{c}_{33} = 6$ GPa, $\bar{c}_{55} = 2$ GPa, $\bar{c}_{66} =$ 11 GPa and $\bar{\rho} = 2113$ kg/m³. The presence of fluids has decreased substantially the velocities and induced considerable shear-wave splitting.

In the following templates (Figures 20-22), we maintain constant the water and organic matter fractions, $\phi_w = 0.05$ and $\phi_{\rm OC} = 0.2$, respectively. Figure 20 and 21 respectively show v_P/v_S as a function of the acoustic impedance (AI) and λ - μ - ρ templates for various values of the gas and oil saturation (solid and dashed lines, respectively). The models are Backus averaging (a) and Gassmann equation (b), the minimum amount of kerogen is 5 % and the frequency is 50 Hz. Wood average to obtain the bulk modulus of the fluid mixture has been used here since the results are similar to those of the White model. Given the values of S_g and S_o , the kerogen content is

$$\mathbf{K} = 100 \ \phi_k = 100 \ \frac{\phi_{\rm OC} - (S_o + S_g)(\phi_{\rm OC} + \phi_w)}{1 - S_o - S_g}.$$
 (11)

In both cases, the main variations occur at low gas saturations and high oil saturations, with the Gassmann equation predicting lower v_P/v_S values, while the λ - μ - ρ templates are very similar. Y- ν (Young modulus-Poisson ratio) templates are shown in Figure 22 for the three Poisson ratios defined in equation (3). The Young modulus is defined in equation (5) and the rock-physics model is Backus averaging.

In order to build templates of the elastic properties at different pore pressures we have to establish a proper model in agreement with experimental data. Pressure effects are modeled with the equations reported in Appendix F, where we assume that the dryrock elasticity constants of the smectite-illite frame (without the water) are affected by the confining and pore pressures. Invoking the effective pressure law (Carcione, 2000a,b; Gei and Carcione, 2003) and assuming that the effective pressure is equal to the differential pressure $p_d = p_c - p$, where p is the pore pressure, the confining pressure can be replaced by the differential pressure and equation (59) is obtained. Vernik (1995, Tables A-1 and A-4) provides experimental data for the Kimmeridge shale useful to evaluate the parameter c. The velocities, corresponding to a shale at 2146 m depth, TOC (wt %) = 1.64 and kerogen content K = 4.37 %, are reported in Table 3. He considers a grain density $\rho_s = 2.71$ g/cm³ and a kerogen density $\rho_k = 1.2$ g/cm³. Using equation (9), the shale density is $\rho = 2.63$ g/cm³. From the data of well 3, we consider a depth of 2880 m, with TOC (wt %) = 5.01, K = 12.32 % and $\rho = 2.5$ g/cm³. Figure 23 shows the velocities as a function of pressure corresponding to the experimental data (a) and to the present model (b), where c = 1.1 in equation (59). This simple model describes properly the pressure behaviour of the shale.

Another approach considers the inverse Gassmann equation (70), which can be implemented if detailed laboratory data is available (see Appendix F). This approach can also be used to perform fluid substitution. To illustrate the method, we consider a sample of Kimmeridge shale fully saturated with kerogen, taken from a depth of 2768 m, whose velocities are given in Table 4 (see Tables A-1 and A-4 in Vernik (1995)). This sample is strongly anisotropic, with $\epsilon = 0.35$ and $\gamma = 0.33$. Based on a grain density $\bar{\rho}_s$ = 2.17 g/cm³ and kerogen properties $v_P = 2.6$ m/s, $v_S = 1.2$ m/s, $\rho_k = 1.4$ g/cm³, the wet-rock elasticity constants obtained with equations (71) are given in Table 4. The kerogen content is K = 40 % and the bulk density is $\rho = 1.862$ g/cm³ (Vernik, 1995). The inversion using equation (70) yields the dry-rock elasticity constants reported in Table 4. The elasticity constants of the smectite-illite-water composite (assumed isotropic) used for the inversion are $c_{33}^s = 16.5$ GPa and $c_{55}^s = 5.5$ GPa, corresponding to a Poisson medium with $v_P = 2.76$ km/s, $v_S = 1.593$ km/s and $\bar{\rho}_s = 2.17$ g/cm³. This choice satisfies the stability conditions. As can be seen in Table 4, the elasticity constants c_{33}^m and c_{55}^m , related to the direction perpendicular to layering, are more affected by changes in the confining pressure, particularly c_{33}^m , whose value is much lower than the wet-rock value. This is due to the high kerogen content as shown by Carcione et al. (2011), who obtained dry-rock elasticity constants for various samples of the Bakken shale.

Using equations (62), (63) and (64), we obtain

$$\hat{c}_{11} = 19.72 \text{ GPa, } \hat{c}_{11} = -0.67 \text{ GPa, } p_{11}^* = 17.73 \text{ MPa,} \\
\hat{c}_{13} = 5.54 \text{ GPa} \quad \hat{c}_{13} = -0.88 \text{ GPa, } p_{13}^* = 22.10 \text{ MPa,} \\
\hat{c}_{33} = 15.98 \text{ GPa, } \hat{c}_{33} = -18.81 \text{ GPa, } p_{33}^* = 15.72 \text{ MPa,} \\
\hat{c}_{55} = 4.40 \text{ GPa, } \hat{c}_{55} = -1.24 \text{ GPa, } p_{55}^* = 27.64 \text{ MPa,} \\
\hat{c}_{66} = 6.87 \text{ GPa, } \hat{c}_{66} = -0.52 \text{ GPa, } p_{66}^* = 19.43 \text{ MPa.}$$
(12)

One could consider the smectite/illite conversion and kerogen/oil/gas generation and the induced pore pressure affecting the rock properties but the objective is to analyse the elastic properties of the shale for varying pore pressure and fixed values of the kerogen content and oil and gas saturations. We then assume that a rock at a given depth is subject to pore pressure changes. In this case, the stiff porosity is constant and pressure affects mainly the dry-rock moduli by closure of microcracks, whose (soft) porosity is negligible compared to the stiff porosity. In a lesser degree, pressure also affects the bulk density, mainly through the gas density. We consider the dry-rock elasticity constants (61) and the parameterization (12), representing the rock frame made of the smectite-illite-water composite "mineral". The depth of this shale is 2768 m and the hydrostatic and confining pressures are $p_H = 28$ and $p_c = 68$ MPa, respectively. Based on the density of the smectite-illite-water composite (2.17 g/cm³) and assuming a proportion of illite of 76 % (according to Figure 4), the smectite-illite density is 2.74 g/cm³, giving a water proportion $\phi_w = 0.2$. We assume $S_o = 0.3$ and $S_g = 0.1$ and since $\phi_{\rm OC} = 0.4$ and using equations (10) and (11), we have $\phi_k = 0.27$ (K = 27 %), $\phi_o = 0.1$ and $\phi_g = 0.033$. Figure 24 shows the dry-rock and wet-rock velocities as a function of the differential pressure ($p_d = p_c - p$) for full kerogen content (a) and $S_o = 0.3$ and $S_g = 0.1$ (b). The bedding-normal P-wave velocity is highly affected by the pore pressure and the presence of fluids. The dry-rock velocities are generally higher due to the density effect.

It is clear that the replacement of kerogen by a lower density material (oil or gas) greatly affects the bedding-normal P-wave modulus. Next, we build templates for different pore pressures and varying oil saturation, assuming no gas. For a given oil saturation S_o , the kerogen content is $K = 100 \ [\phi_{OC} - S_o(\phi_{OC} + \phi_w)]/(1 - S_o)$, which has to be greater than zero. This happens for $S_o \leq \phi_{OC}/(\phi_{OC} + \phi_w) = 0.66$ in this case. We have K = 40 % at $S_o = 0$ and K = 10 % at $S_o = 0.6$. Figure 25 shows v_P/v_S (v_{33}/v_{55}) as a function of the acoustic impedance (AI) (a) and the λ - μ - ρ template for different values of the pore pressure and varying oil saturation. The model is Gassmann equation and the frequency is 50 Hz. Unlike the case of varying gas saturation (see Figures 20 and 21), the λ - μ - ρ template seems to discriminate the different pore pressures better than v_P/v_S versus acoustic impedance.

Finally, we consider a transversely isotropic shale layer of thickness h at 2 km and 3 km containing kerogen and gas embedded in a homogeneous isotropic shale without organic matter (see Figure 26). The elastic properties of the homogeneous medium (smectite-illite-water composite with $\phi_w = 0.05$) at 2 km depth are $c_{33}^s = 20.5$ GPa, c_{55}^s = 6.2 GPa and $\bar{\rho}_s = 2.398$ g/cm³, according to the smectite/illite conversion considered above. It is $v_P = 2.92$ km/s and $v_S = 1.61$ km/s. We assume h = 25 m, smaller than the dominant wavelengths of the P and S waves, which are approximately 97 m and 53 m, respectively, for a frequency of 30 Hz. The elastic properties of the smectite-illitewater composite ($\phi_w = 0.05$) of the source rock are $c_{11}^s = 35$ GPa, $c_{13}^s = 7.4$ GPa, $c_{33}^s = 20.5$ GPa, $c_{55}^s = 6.2$ GPa, $c_{66}^s = 11.9$ GPa and $\bar{\rho}_s = 2.398$ g/cm³. According to Krief equations (56) and an organic matter content $\phi_{OC} = 0.25$ (maximum value in Figure 6), the elastic properties of the frame are $c_{11}^m = 24.6$ GPa, $c_{13}^m = 2.9$ GPa, $c_{33}^m = 8.1$ GPa, $c_{55}^m = 2.5$ GPa and $c_{66}^m = 8.4$ GPa.

The elastic properties of the homogeneous medium (smectite-illite-water composite with $\phi_w = 0.05$) at 3 km depth are $c_{33}^s = 35$ GPa, $c_{55}^s = 11$ GPa and $\bar{\rho}_s = 2.691$ g/cm³, according to the smectite/illite conversion considered above. It is $v_P = 4.6$ km/s and $v_S = 3.6$ km/s. The dominant wavelengths of the P and S waves are approximately 153 m and 120 m, respectively. The elastic properties of the smectite-illite-water composite ($\phi_w = 0.05$) of the source rock are $c_{11}^s = 57.3$ GPa, $c_{13}^s = 12.6$ GPa, $c_{33}^s = 35$ GPa, c_{55}^s = 11 GPa, $c_{66}^s = 19.5$ GPa and $\bar{\rho}_s = 2.691$ g/cm³. According to Krief equations (56) and an organic matter content $\phi_{OC} = 0.25$ (maximum value in Figure 6), the elastic properties of the frame are $c_{11}^m = 40.1$ GPa, $c_{13}^m = 4.8$ GPa, $c_{33}^m = 13$. GPa, $c_{55}^m = 4.2$ GPa and $c_{66}^m = 13.6$ GPa.

Regarding the pore infill material, the kerogen and gas properties are those given in Table 1 at 3 km depth. For a given gas saturation S_o , the kerogen content is K = $100 \ [\phi_{\rm OC} - S_g(\phi_{\rm OC} + \phi_w)]/(1 - S_g)$, which has to be greater than zero. This happens for $S_g \leq \phi_{\rm OC}/(\phi_{\rm OC} + \phi_w) = 0.83$ in this case. Gas saturation can be defined as $S_g = \phi_g/(\phi_g + \phi_w)$ (the definition so far) or $S'_g = \phi_g/(\phi_g + \phi_k)$ if we consider the organic pore infill. They are related as $S'_g = \phi_w S_g/[\phi_{\rm OC}(1 - S_g)] < 0.97$. Figure 27 shows the real part of the reflection and transmission coefficients at 2 km (a) and 3 km (b) for a frequency of 30 Hz and a saturation $S_g = 0.2$ (for this saturation $S'_g = S_g$). The intercept and gradient for various values of the gas saturation and kerogen content are given in Table 5 and the data is represented in Figure 28, where it is clear that in all the cases the AVO is class IV (Castagna and Swan, 1997). Yenugu and Han (2013) have also obtained a class IV AVO, but they compute the seismic response of a single interface consisting of Bakken shale overlain by a high velocity limestone. Also, the reflection coefficient (intercept) is increasing with maturity.

6 Conclusions

We propose a modeling methodology to build different rock-physics templates for source rocks containing organic matter, specifically, kerogen, oil and gas. The fundamental aspects of shale oil and shale gas evolution from shales fully saturated with kerogen are considered by modeling the hydrocarbon generation and mineral diagenesis as a function of pressure, temperature and burial depth. The rock-physics models are based on two dissimilar approaches, namely, Backus averaging and Gassmann equation, which yield similar results in general, indicating the robustness of the methodology. Rockphysics templates are built which are useful to evaluate kerogen content, hydrocarbon saturations and in-situ pore pressure. Mesoscopic-loss effects due to partial fluid saturations affecting wave velocities are considered, but the Wood average is almost equivalent at seismic frequencies .

The creation of rock-physics templates for an specific site requires calibration with well logs and information from related reports. This is performed for the Spekk formation at the North Sea, where the Kimmeridge shale is the main unit. Basically, the analysis is based on TOC values as a function of depth, which allows us to evaluate the kerogen content, and sonic and density logs to quantify the elastic properties of the minerals and shale frame. In the calibration process, at full kerogen saturation, Backus averaging and Gassmann equation give practically the same results. Differences can be observed in the presence of hydrocarbon fluids, with Backus averaging predicting lower normal-bedding velocity at zero kerogen content, indicating that this model provides lower and upper limits. The main variations in the templates occur at low gas saturations and high oil saturations, with the Gassmann equation predicting lower v_P/v_S values, while the λ - μ - ρ templates are very similar. Wavefront representations indicate that the presence of fluids has decreased substantially the velocities and induce considerable shear-wave splitting.

Pore pressure affects mainly the elasticity constants of the shale frame and in a lesser degree the bulk density through the gas density, whose changes with pore pressure are more remarkable than those of water and oil. We consider an specific sample of Kimmeridge shale to investigate the pressure effects. The bedding-normal P-wave velocity is highly affected by the pore pressure and the presence of fluids and the dry-rock velocities are generally higher due to the density effect. Unlike the case of varying gas saturation, the λ - μ - ρ template seems to discriminate the different pore pressures better than v_P/v_S versus acoustic impedance, mainly when pore pressure approaches the fracture pressure (or the confining pressure). Finally, we have computed the reflection coefficient of a thin shale layer at a given depth saturated with kerogen and gas. The calculations indicate that the AVO behavior is class IV for any value of the gas saturation.

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A Oil/gas generation and shale diagenesis

Let us assume a source rock at depth z. The lithostatic pressure for an average sediment density $\bar{\rho}$ is $p_c = \bar{\rho}gz$, where g is the acceleration of gravity. On the other hand, the hydrostatic pore pressure is approximately $p_H = \bar{\rho}_w gz$, where $\bar{\rho}_w$ is the density of water. For a constant sediment burial rate, S, and a constant geothermal gradient, G, the temperature variation of a particular sediment volume is

$$T = T_0 + Gz = T_0 + Ht, \quad z = St, \quad H = GS$$
 (13)

with a surface temperature T_0 at time t = 0, where t is deposition time. Typical values of G range from 20 to 40 °C/km, while S may range between 0.02 and 0.5 km/m.y. (m.y. = million years).

A.1 Kerogen/oil/gas conversion and overpressure

Assume that at time t = 0, corresponding to the surface, the shale contains kerogen at temperature T_0 and that the volume is "closed". The mass of convertible kerogen changes with deposition time t at a rate proportional to the mass present. Assuming a first-order kinetic reaction with the reaction rate given by the Arrhenius equation (Pepper and Corvi, 1995;

Carcione, 2000; Pinna et al, 2011), the fraction of kerogen converted to oil (or fluid saturation, s) satisfies the following equation

$$\frac{\partial s}{\partial t} = -sA \exp([-E/RT(t)]), \tag{14}$$

where E is the activation energy, R = 1.986 cal/(mol °K) is the gas constant, A is the reaction rate at infinite temperature and T(t) is the absolute temperature. The solution is given below.

Let us obtain now the geopressure generated by the conversion of kerogen to oil in the presence of water (brine) in the pore space. We define the excess pore pressure by $\Delta p = p - p_i$, where p_i is the initial pore pressure and p is the pore pressure when a fraction s of kerogen mass has been converted to oil. Assume that the initial volumes of kerogen, water and pore space are V_{ki} , V_{wi} and V_{pi} , respectively. The definition of the respective bulk moduli are

$$K_o = -V_o \frac{dp}{dV_o}, \quad K_k = -V_k \frac{dp}{dV_k}, \quad K_w = -V_w \frac{dp}{dV_w}, \quad K_p = +V_p \frac{dp}{dV_p}, \tag{15}$$

where V_o is the oil volume equivalent to the amount of converted kerogen. The + sign means that the pore volume increases with increasing pore pressure, since K_p is the bulk modulus at constant confining pressure. Integration of equations (15) yields

$$V_o(p) = V_{oi} \exp(-\Delta p/K_o), \quad V_k(p) = V_{ki} \exp(-\Delta p/K_k),$$

$$V_w(p) = V_{wi} \exp(-\Delta p/K_w), \quad V_p(p) = V_{ki} \exp(+\Delta p/K_p).$$
(16)

Since the mass balance is independent of pressure, the amount of converted oil can be expressed as

$$\rho_o V_{oi} = s \rho_k V_{ki},\tag{17}$$

where ρ_o is the oil density, and V_{oi} and V_{ki} are the oil and kerogen volumes at p_i .

The pore volume at the initial pore pressure is $V_{pi} = V_{ki} + V_{wi}$ and the initial water saturation is $S_w = V_{wi}/V_{pi}$. Using (17), the oil volume becomes

$$V_o(p) = sDV_{ki} \exp(-\Delta p/K_o), \qquad (18)$$

where $D = \rho_k / \rho_o$. Since at pressure p the pore space volume is

$$V_p = (1 - s)V_k + V_o + V_w, (19)$$

we obtain

$$s = \frac{S_w \exp(-\Delta p/K_w) + (1 - S_w) \exp(-\Delta p/K_k) - \exp(\Delta p/K_p)}{(1 - S_w)[\exp(-\Delta p/K_k) - D\exp(-\Delta p/K_o)]}.$$
 (20)

This equation is equivalent to (A13) in Carcione (2000), which has a typographical error, since the coefficient in the third exponential of the numerator is c_k instead of c_p .

The shale studied here is located at 3 km depth. The lithostatic pressure at this depth, for an average density of $\bar{\rho} = 2.4 \text{ g/cm}^{-3}$ is equal to $\bar{\rho}gz \simeq 70$ MPa, where g is the acceleration of gravity. On the other hand, the hydrostatic pore pressure is approximately 30 MPa. Thus, the maximum possible pore pressure change Δp will be from hydrostatic to lithostatic, i.e., nearly 40 MPa (at this excess pressure, the rock may reach the fracturing stage). Since, under these conditions, the arguments in the exponential functions in equation (20) are much less than one, these functions can be approximated by $\exp(x) \simeq 1 + x$, $x \ll 1$, giving

$$\Delta p = \frac{s(1 - S_w)(D - 1)}{K_p^{-1} + K_k^{-1} + s(1 - S_w)(K_o^{-1}D - K_k^{-1}) - S_w(K_k^{-1} - K_w^{-1})}.$$
(21)

Neglecting the mineral compressibility, the pore space bulk modulus is given by $K_p = \phi K_m$, where K_m is the bulk modulus of the frame (see equation (7.76) in Carcione (2007)). Here, we consider that the pore-space bulk modulus depends linearly with the porosity as

$$K_p[\text{MPa}] = 2400 - 5400\phi'$$
 (22)

(Carcione, 2000), where $\phi' = \phi_k + \phi_w$ is the initial kerogen plus water proportion. Pore-space incompressibilities range from 240 to 2400 MPa, which correspond to compliant and rigid rocks, respectively.

A.2 Smectite/illite conversion

Pytte and Reynolds (1989) propose a model for the smectite/illite ratio r based on the $n {\rm th-order}$ Arrhenius-type reaction

$$\frac{\partial r}{\partial t} = -r^n A \exp(-E/RT(t)), \tag{23}$$

where r is the smectite/illite ratio. The illite/smectite ratio in percent is 100 (1 - r). The solution of equation (23) is given in the next section.

Smectite is assumed isotropic and it is mixed with illite by using Backus averaging (66) to obtain the elasticity constants of the mineral composing the frame.

A.3 Solutions

Equations (14) and (23) are of the form

$$\frac{\partial y}{\partial t} = -y^n A \exp(-E/RT(t)), \qquad (24)$$

which has the solution

$$y(t) = m^{-1/m} \left\{ \frac{y_0^{-m}}{m} + \frac{A}{H} \left[\frac{E}{R} \left[\text{Ei}(x) - \text{Ei}(x_0) \right] + T \exp(x) - T_0 \exp(x_0) \right] \right\}^{-1/m}, \quad (25)$$

where m = n - 1, Ei (x) is the exponential integral,

$$x = -\frac{E}{RT}, \quad x_0 = -\frac{E}{RT_0}.$$
 (26)

where the dependence on the deposition time is given in the absolute temperature (see equation (13)).

The solution of equation (14) $(n = 1, s_0 = 1)$ simplifies to

$$s = 1 - \exp\left\{-\frac{A}{H}\left[TE_2(-x) - T_0E_2(-x_0)\right]\right\},$$
(27)

where

$$E_j(x) = \int_1^\infty \exp(-xq) \frac{dq}{q^j}.$$
(28)

Equation (25) can also be evaluated with E_1 using the relation $Ei(x) = -E_1(-x)$. Approximations to equation (27) can be found in Berg and Gangi (1999), Carcione (2000) and Pinna et al. (2011).

B Properties of hydrocarbon gas

In-situ reservoir gas behaves as a real gas, which satisfies approximately the van der Waals equation (Friedman, 1963):

$$(p+a\rho_q^2)(1-b\rho_g) = \rho_g R(T+273),$$
(29)

where p is the gas pressure and ρ_g is the gas density. For CH₄, a = 0.225 Pa $(m^3/\text{mole})^2 = 879.9$ Pa $(m^3/\text{kg})^2$ and b = 42.7 cm³/mole $= 2.675 \times 10^{-3}$ m³/kg (one mole of methane corresponds to a mass of 16 g). The critical pressure and temperature are $p_{cr} = 4.6$ MPa and $T_{cr} = -82.7$ °C, respectively. Equation (29) gives the gas density as a function of pressure and temperature, which can be related to depth, if we assume that the gas pressure is equal to the expected formation pressure.

The isothermal gas compressibility c_T depends on pressure. It can be calculated from the van der Waals equation using

$$c_T = \frac{1}{\rho_g} \frac{\partial \rho_g}{\partial p},\tag{30}$$

which gives

$$c_T = \left[\frac{\rho_g R(T+273)}{(1-b\rho_g)^2} - 2a\rho_g^2\right]^{-1}.$$
(31)

For sound waves below 1 GHz or so, it is a better approximation to assume that the compression is adiabatic, i.e., that the entropy content of the gas remains nearly constant during the compression (Morse and Ingard, 1986). Adiabatic compressibility c_S is related to isothermal compressibility c_T by $c_S = c_T/\gamma$, where γ is the heat capacity ratio at constant pressure, which depends on measurable quantities (Morse and Ingard, 1986). Batzle and Wang (1992) provide an empirical equation

$$\gamma = 0.85 + \frac{5.6}{p_r + 2} + \frac{27.1}{\left(p_r + 3.5\right)^2} - 8.7 \exp\left[-0.65\left(p_r + 1\right)\right],\tag{32}$$

where $p_r = p/p_{cr}$ is the reduced pressure. In this case, the gas bulk modulus can expressed as

$$K_g = \frac{1}{c_S} = \frac{\gamma}{c_T}.$$
(33)

C Properties of oil and brine

The liquid properties depend on temperature and pressure and on API number and salinity, if the fluid is oil or water, respectively. Batzle and Wang (1992) and Mavko et al. (2009) provide a series of useful empirical relations between the state variables and velocity and density. For completeness we give these relations here. The equations are limited to the pressures and temperatures of the experiments made by Batzle and Wang (1992) (around 60 MPa and 100 o C).

Oil density (in g/cm³) versus temperature T (in ${}^o\mathrm{C})$ and pressure p (in MPa) can be expressed as

$$\rho_o = \frac{\rho_0 + (0.00277p - 1.71 \times 10^{-7} p^3)(\rho_0 - 1.15)^2 + 3.49 \times 10^{-4} p}{0.972 + 3.81 \times 10^{-4} (T + 17.78)^{1.175}},$$
(34)

where ρ_0 is the density at 15.6 $^o\mathrm{C}$ and atmospheric pressure. This density is related to API gravity by

$$API = \frac{141.5}{\rho_0} - 131.5.$$
(35)

The expression relating wave velocity of dead oil (oil with no dissolved gas) to pressure, temperature and API gravity is

$$V_o = 15450 \ (77.1 + \text{API})^{-1/2} - 3.7T + 4.64p + 0.0115 \ (0.36 \ \text{API}^{1/2} - 1)Tp, \tag{36}$$

where V_o is given in m/s and p in MPa. Using these relationships, we get the oil bulk modulus as $K_o = \rho_o V_o^2$.

The density of brine in g/cm^3 is given by

$$\rho_w = \rho'_w + s_c \{ 0.668 + 0.44 s_c + 10^{-6} [300p - 2400p s_c + T(80 + 3T - 3300 s_c - 13p + 47p s_c)] \},$$
(37)

with

$$\rho'_w = 1 + 10^{-6} (-80T - 3.3T^2 + 0.00175T^3 + 489p - 2Tp + 0.016T^2p -1.3 \times 10^{-5}T^3p - 0.333p^2 - 0.002Tp^2),$$
(38)

where s_c is the weight fraction (ppm/1000000) of sodium chloride. Finally, the velocity function for brine is

$$V_w = V'_w + s_c(1170 - 9.6T + 0.055T^2 - 8.5 \times 10^{-5}T^3 + 2.6p - 0.0029Tp$$

$$-0.0476p^{2}) + s_{c}^{1.5}(780 - 10p + 0.16p^{2}) - 1820s_{c}^{2},$$
(39)

where V'_w is the velocity of pure water given by

$$V'_w = \sum_{i=0}^4 \sum_{j=0}^3 w_{ij} T^i p^j,$$
(40)

with constants w_{ij} given in Table 2. Using these relationships, we get the brine bulk modulus as $K_w = \rho_w V_w^2$.

D Effective fluid model for partial gas saturation

The mixture oil-gas behaves as a composite fluid with properties depending on the constants of the constituents and their relative concentrations. The simplest solution to obtain its bulk modulus is to assume the Wood average:

$$K_f = \left(\frac{s_g}{K_g} + \frac{s_o}{K_o}\right)^{-1},\tag{41}$$

where $s_g = \phi_g/(\phi_g + \phi_o)$ denotes the gas saturation and $s_o = 1 - s_g$ is the oil saturation. Equation (41) corresponds to the low-frequency limit. The density is

$$\rho_f = s_g \rho_g + s_o \rho_o. \tag{42}$$

When the fluids are not mixed in the pore volume, but distributed in patches, the effective bulk modulus of the composite fluid is higher than that predicted by Wood equation. We assume a simplified model where the frame is the kerogen and the fluids are oil and gas. White (1975) assumed spherical patches much larger than the grains but much smaller than the wavelength. He developed the theory for a gas-filled sphere of porous medium of radius r_0 located inside a water-filled sphere of porous medium of outer radius r_1 ($r_0 < r_1$). The saturation of gas is

$$s_g = \frac{r_0^3}{r_1^3}, \quad s_o = 1 - s_g. \tag{43}$$

For simplicity, let us redefine the saturation and density of gas and oil by S_1 and S_2 and ρ_{f1} and ρ_{f2} , respectively.

The permeability, κ , of the kerogen frame depends on the fluid content. We assume a Kozeny-Carman form

$$\kappa = \frac{2\kappa_0\varphi^3}{(1-\varphi)^2} \tag{44}$$

(Mavko et al. 2009), where $\varphi = \phi_f/(\phi_f + \phi_k)$, where κ_0 is a reference value at 50 % fluid saturation ($\varphi = 0.5$); in this work we assume $\kappa_0 = 2.5$ D.

The bulk modulus of the kerogen-oil-gas mixture is then given by

$$K_W \simeq \operatorname{Re}(K^*) \tag{45}$$

(Carcione, 2007), where "Re" denotes de real part and

$$K^* = \frac{K_\infty}{1 - K_\infty W},\tag{46}$$

where

$$W = \frac{3ir_{0}\kappa(R_{1} - R_{2})}{r_{1}^{3}\omega(\eta_{1}Z_{1} - \eta_{2}Z_{2})} \left(\frac{K_{A1}}{K_{1}} - \frac{K_{A2}}{K_{2}}\right),$$

$$R_{1} = \frac{(K_{1} - K_{m})(3K_{2} + 4\mu_{m})}{K_{2}(3K_{1} + 4\mu_{m}) + 4\mu_{m}(K_{1} - K_{2})S_{1}},$$

$$R_{2} = \frac{(K_{2} - K_{m})(3K_{1} + 4\mu_{m})}{K_{2}(3K_{1} + 4\mu_{m}) + 4\mu_{m}(K_{1} - K_{2})S_{1}},$$

$$Z_{1} = \frac{1 - \exp(-2\gamma_{1}r_{0})}{(\gamma_{1}r_{0} - 1) + (\gamma_{1}r_{0} + 1)\exp(-2\gamma_{1}r_{0})},$$

$$Z_{2} = \frac{(\gamma_{2}r_{1} + 1) + (\gamma_{2}r_{1} - 1)\exp[2\gamma_{2}(r_{1} - r_{0})]}{(\gamma_{2}r_{1} + 1)(\gamma_{2}r_{0} - 1) - (\gamma_{2}r_{1} - 1)(\gamma_{2}r_{0} + 1)\exp[2\gamma_{2}(r_{1} - r_{0})]},$$

$$K_{Ej} = \left[1 - \frac{\alpha K_{fj}(1 - K_{j}/K_{s})}{\varphi K_{j}(1 - K_{fj}/K_{s})}\right] K_{Aj},$$

$$K_{Aj} = \left[\frac{\varphi}{K_{fj}} + \frac{1}{K_{s}}(\alpha - \varphi)\right]^{-1}, \quad j = 1, 2,$$

$$\alpha = 1 - \frac{K_{m}}{K_{s}},$$

$$(47)$$

 K_s is the bulk modulus of the kerogen (see below), K_{fj} are the bulk moduli of the fluids, η_j are the fluid viscosities, K_m and μ_m are given by Krief equations

$$K_m = K_k (1 - \varphi)^{3/(1 - \varphi)} \quad \text{and} \quad \mu_m = K_m \mu_k / K_k \tag{48}$$

(Krief et al., 1990). Moreover,

$$K_{\infty} = \frac{K_2(3K_1 + 4\mu_m) + 4\mu_m(K_1 - K_2)S_1}{(3K_1 + 4\mu_m) - 3(K_1 - K_2)S_1}$$
(49)

is the – high frequency – bulk modulus when there is no fluid flow between the patches. K_1 and K_2 are the – low frequency – Gassmann moduli, which are obtained as

$$K_{j} = \frac{K_{s} - K_{m} + \varphi K_{m} \left(K_{s} / K_{fj} - 1 \right)}{1 - \varphi - K_{m} / K_{s} + \varphi K_{s} / K_{fj}}, \quad j = 1, 2.$$
(50)

For values of the gas saturation higher than 52 %, or values of the oil saturation between 0 and 48 %, the theory is not rigorously valid. Another limitation to consider is that the size of gas pockets should be much smaller than the wavelength.

To obtain the effective fluid modulus K_f due to mesoscopic anelastic effects we consider Gassmann equation

$$K_W = \frac{K_s - K_m + \varphi K_m \left(K_s / K_f - 1\right)}{1 - \varphi - K_m / K_s + \varphi K_s / K_f}.$$
(51)

and solve for K_f :

$$K_{f} = \frac{\varphi K_{s}(K_{W} - K_{m})}{K_{s} - (1 + \varphi)K_{m} - K_{W}(1 - \varphi - K_{m}/K_{s})}.$$
(52)

If φ exceeds a critical porosity value, say 0.5, K_f is the Wood modulus, since the iso-stress condition holds.

E Properties of the kerogen/fluid mixture

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The stiffnesses of the kerogen/fluid mixture can be calculated by using the model developed by Kuster and Toksöz (1974). If $s_f = \phi_f/(\phi_f + \phi_k)$ is the fluid saturation, the stiffnesses are

$$\frac{c_{13}^{i\,j} + \frac{2}{3}c_{55}^{i\,j}}{K_k} = \frac{1 + [4\mu_k(K_f - K_k)/(3K_f + 4\mu_k)K_k]s_f}{1 - [3(K_f - K_k)/(3K_f + 4\mu_k)]s_f}$$
(53)

and

$$\frac{c_{55}^{if}}{\mu_k} = \frac{(1-s_f)(9K_f + 8\mu_k)}{9K_k + 8\mu_k + S(6K_k + 12\mu_k)}.$$
(54)

The density of the mixture is simply $\rho_{if} = (\phi_k \rho_k + \phi_f \rho_f)/(\phi_k + \phi_f)$.

F Dry-rock elasticity constants

Gassmann equation requires the knowledge of the dry-rock elasticity constants. Krief et al. (1990) propose a simple heuristic equation:

$$K_m = K_s (1-\phi)^{A/(1-\phi)}$$
 and $\mu_m = K_m \mu_s / K_s$, (55)

where A is a constant which depends on the type of rock (the second expression in equation (55) is assumed here). The porosity dependence is consistent with the concept of critical porosity, since the moduli should be small above a certain value of the porosity (usually between 0.4 and 0.6) (Mavko and Mukerji, 1998).

The properties of the frame can be described by an anisotropic version of the Krief model:

where

$$g(x) = (1 - \phi)^{x/(1 - \phi)}$$
(57)

and A and B are constants. The use of two constants is somehow equivalent to vary the Krief exponent as a function of the propagation (phase) angle, since c_{11}^m and c_{66}^m describe the velocities along the stratification, and c_{33}^m and c_{55}^m along the perpendicular direction. As we shall see in the example, A < B, indicating that the critical porosity value is larger for the elastic constants describing the properties along the layering, i.e., the skeleton is mainly defined by these constants at high porosity. Equations (56) reduce to equation (55) for A = B in the isotropic case. Another possibility is to obtain the dry-rock elasticity constants from wet-rock data by using the inverse Gassmann relation (70) (see Carcione et al., 2011).

F.1 Pressure effect. Model 1

A suitable model of the elasticity constants of the smectite-illite frame as a function of the pore and confining pressure can be expressed as

$$c_{11}^{nn} = c_{11}^{s}g(A)h(p), c_{66}^{nn} = c_{66}^{s}g(A)h(p), c_{13}^{nn} = c_{13}^{s}g(B)h(p), c_{33}^{nn} = c_{33}^{s}g(B)h(p), c_{55}^{nn} = c_{55}^{s}g(B)h(p),$$
(58)

where p is the pore pressure,

$$h(p) = c \left[1 - \exp[-(p_c - p)/p^*] \right], \tag{59}$$

 p_c is the confining pressure,

$$p^* = -\frac{p_H - p_c}{\ln(1 - 1/c)},\tag{60}$$

 p_H is the hydrostatic pressure and c > 1 is a parameter obtained by fitting experimental data. Function h has the following properties: $h(p = 0) = c[1 - \exp(-p_c/p^*)]$, $h(p = p_H) = 1$ and $h(p = p_c) = 0$, where the last property means that the rock is completely unconsolidated in the absence of a confining pressure. Before this happens, at $p_{\rm fr} < p_c$, fracture occurs, where $p_{\rm fr}$ is the fracture pressure. For simplicity the pressure effects are "isotropic". The pressure dependence (59) is theoretically justified by Kaselow and Shapiro (2004) and experimental results (Carcione and Gangi, 2000a,b).

This model is the simplest possible since it is based in a single parameter (c) which can easily be estimated from experimental data.

F.2 Pressure effect. Model 2

A model completely based on data can be obtained by using equation (70) below. We use this equation to obtain the dry-rock stiffness constants from experimental data with 100 % kerogen occupying the pore space, and assuming an exponential dependence on the differential pressure p_d (Kaselow and Shapiro, 2004),

$$c_{IJ}^{m} = \hat{c}_{IJ} + \check{c}_{IJ} \exp(-p_d/p_{IJ}^*), \tag{61}$$

where $p_d = p_c - p_H$. The parameters \hat{c}_{IJ} , \hat{c}_{IJ} and p_{IJ}^* are obtained from the data using the stiffnesses at three different confining pressures and assuming an effective pressure law, i.e., replacing p_d by p_c (with $p_H = 0$), equation (61) should give the same value of the elasticity constants (e.g., Gei and Carcione, 2003). If from the experimental data (e.g., Vernik, 1995), we have the sets $c_{IJ}^{(1)}$, $c_{IJ}^{(2)}$ and $c_{IJ}^{(3)}$, at p_{c1} , p_{c2} and p_{c3} , we obtain the unknown parameters from

$$\check{c}_{IJ} = \frac{c_{IJ}^{(3)} - c_{IJ}^{(1)}}{\exp(-p_{c3}/p_{IJ}^*) - \exp(-p_{c1}/p_{IJ}^*)},\tag{62}$$

$$\hat{c}_{IJ} = c_{IJ}^{(1)} - \check{c}_{IJ} \exp(-p_{c1}/p_{IJ}^*),$$
(63)

and

$$(c_{IJ}^{(3)} - c_{IJ}^{(1)}) \exp[(p_{c1} + p_{c3})/p_{IJ}^*] + (c_{IJ}^{(1)} - c_{IJ}^{(2)}) \exp[(p_{c1} + p_{c2})/p_{IJ}^*] + (c_{IJ}^{(2)} - c_{IJ}^{(3)}) \exp[(p_{c2} + p_{c3})/p_{IJ}^*] = 0.$$
(64)

The dry-rock elasticity constants should satisfy the conditions of physical stability. For a transversely isotropic medium these are

$$c_{11}^m > |c_{12}^m|, \quad (c_{11}^m + c_{12}^m)c_{33}^m > 2(c_{13}^m)^2, \quad c_{55}^m > 0$$
 (65)

(e.g., Carcione, 2007). The elasticity constants of the mineral grains, c_{IJ}^s (smectite-illite-water in this case), are constrained by these conditions We assume isotropy ($c_{11}^s = c_{33}^s$, $c_{66}^s = c_{55}^s$, $c_{12}^s = c_{13}^s = c_{11}^s - 2c_{66}^s$) and a Poisson medium ($c_{13}^s = c_{55}^s$) and then choose the medium with maximum stiffness satisfying equation (70).

G Petro-elastical models

G.1 Wet-rock Backus velocities

Following Vernik and Nur (1992) and Carcione (2000), we assume that the rock is a multilayer composite made of smectite-illite-water and kerogen-hydrocarbon fluid (see Figures 1a and 1b). Backus averaging gives a transversely isotropic equivalent medium described by five stiffness constants \bar{c}_{IJ} , where

$$\bar{c}_{11} = \langle c_{11} - c_{13}^2 c_{33}^{-1} \rangle + \langle c_{33}^{-1} \rangle^{-1} \langle c_{33}^{-1} c_{13} \rangle^2
\bar{c}_{33} = \langle c_{33}^{-1} \rangle^{-1}
\bar{c}_{13} = \langle c_{33}^{-1} \rangle^{-1} \langle c_{33}^{-1} c_{13} \rangle
\bar{c}_{55} = \langle c_{55}^{-1} \rangle^{-1}
\bar{c}_{66} = \langle c_{66} \rangle,$$
(66)

(Schoenberg and Muir, 1989; Carcione, 2007), with c_{IJ} the complex stifnesses corresponding to the single constituents and $\langle \cdot \rangle$ indicating the weighted average. The proportion of the kerogen-oil-gas mixture is $\phi_k + \phi_f = \phi_k + \phi_o + \phi_g$ and the proportion of smectite-illite-water is $\phi_s + \phi_w$. Porosity is $\phi = \phi_w + \phi_o + \phi_g$.

Since Backus averaging overestimates the experimental velocities at the layering plane, we modify the elasticity constants of smectite-illite-water, which has a lenticular textural pattern (Vernik and Nur, 1992; Carcione, 2000). We assume that only the stiffnesses "parallel to bedding" are affected, with the elasticity constants obtained as $\langle c_{11} \rangle$ and $\langle c_{66} \rangle$, which incorporate the respective local constants of both smectite-illite-water and kerogen.

The wave velocities of the shale are

where P and S denote P and S waves, respectively, and 0 and 90 correspond to propagation perpendicular to and along the layering.

The bulk density is given by

$$\rho = \phi_s \rho_s + \phi_w \rho_w + \phi_k \rho_k + \phi_f \rho_f. \tag{68}$$

G.2 Wet-rock Gassmann velocities

Ciz and Shapiro (2007) obtained the undrained compliance tensor when the pore infill and solid grains are anisotropic materials,

$$\bar{s}_{ijkl} = s^m_{ijkl} - (s^m_{ijmn} - s^s_{ijmn}) [\phi(\mathbf{s}^{if} - \mathbf{s}^{\phi}) + \mathbf{s}^m - \mathbf{s}^s]^{-1}_{mnqp} (s^m_{qpkl} - s^s_{qpkl}),$$
(69)

where the s's are the components of the compliance tensor, and the Einstein summation is assumed over 1, 2 and 3. Tensor and matrices are denoted with a bold font (see Carcione et al. (2001a,b) for corrections to equation (69)). The compliance tensor \mathbf{s}^{ϕ} is explicitly defined in Ciz and Shapiro (2007). In the case that the skeleton is made of a homogeneous material, $\mathbf{s}^{\phi} = \mathbf{s}^{s}$. For transverse isotropy, we use the following relations between the Voigt stiffnesses and compliances: $c_{11}+c_{12}=s_{33}/s, c_{11}-c_{12}=1/(s_{11}-s_{12}), c_{13}=-s_{13}/s, c_{33}=(s_{11}+s_{12})/s,$ $c_{55}=1/s_{55}$, where $s=s_{33}(s_{11}+s_{12})-2s_{13}^{2}$. The equations for the inversion are obtained by interchanging all c's and s's. Note the following relations: $s_{66}=4s_{1212}$ and $s_{55}=4s_{1313}$, valid for all the compliance tensors, while $c_{66}=c_{1212}$ and $c_{55}=c_{1313}$. The components of the corresponding matrices in the undrained case transform in the same way. Moreover, the usual symmetry relations by interchanging the indices hold (e.g., Carcione, 2007).

Equation (69) can be inverted to obtain the dry-rock compliance tensor as a function of the undrained compliance tensor. We have

$$s_{ijkl}^{m} = s_{ijkl}^{s} + \phi(\bar{s}_{ijmn} - s_{ijmn}^{s})[\phi(\mathbf{s}^{if} - \mathbf{s}^{\phi}) - \bar{\mathbf{s}} + \mathbf{s}^{s}]_{mnqp}^{-1}(s_{qpkl}^{if} - s_{qpkl}^{\phi}).$$
(70)

This equation can be used to obtain the drained compliance tensor by using calibration data (seismic, well or laboratory data).

The wet-rock elasticity constants are related to the phase velocities at 0, 90 and 45 degrees as

$$\bar{c}_{33} = \rho v_P^2 \rho(0),
\bar{c}_{11} = \rho v_P^2 \rho(90),
\bar{c}_{55} = \rho v_S^2(0),
\bar{c}_{66} = \rho v_S^2(90),
\bar{c}_{12} = 2\bar{c}_{66} - \bar{c}_{11},
\bar{c}_{13} = -\bar{c}_{55} + \sqrt{4\rho^2 v_P^4 (45) - 2\rho v_P^2 (45)(\bar{c}_{11} + \bar{c}_{33} + 2\bar{c}_{55}) + (\bar{c}_{11} + \bar{c}_{55})(\bar{c}_{33} + \bar{c}_{55})}$$
(71)

(e.g., Carcione, 2007).

H Energy velocity and wavefront

Let us consider the (x, z)-plane of a transversely isotropic medium and define the direction cosines $l_1 = \sin \theta$ and $l_3 = \cos \theta$, where θ is the phase angle between the symmetry axis and the propagation direction. The expression of the energy velocities of the wave modes can be found for instance in Carcione (2007). The energy velocity vector of the SH wave is

$$\mathbf{v}_e(\text{SH}) = \frac{1}{\rho v_p} (c_{66} l_1 \hat{\mathbf{e}}_1 + c_{55} l_3 \hat{\mathbf{e}}_3), \tag{72}$$

where

$$v_p(\mathrm{SH}) = \sqrt{(\rho)^{-1}(c_{66}l_1^2 + c_{55}l_3^2)}$$
 (73)

is the phase velocity.

The energy velocity components of the qP and qSV waves are

$$v_{e1} = \left(\frac{l_1}{v_p}\right) \frac{(\Gamma_{33} - \rho v_p^2)c_{11} + (\Gamma_{11} - \rho v_p^2)c_{55} - (c_{13} + c_{55})^2 l_3^2}{\rho(\Gamma_{11} + \Gamma_{33} - 2\rho v_p^2)}$$
(74)

and

$$v_{e3} = \left(\frac{l_3}{v_p}\right) \frac{(\Gamma_{33} - \rho v_p^2)c_{55} + (\Gamma_{11} - \rho v_p^2)c_{33} - (c_{13} + c_{55})^2 l_1^2}{\rho(\Gamma_{11} + \Gamma_{33} - 2\rho v_p^2)},\tag{75}$$

where

$$v_{p}(qSV) = (2\rho)^{-1/2} \sqrt{c_{11}l_{1}^{2} + c_{33}l_{3}^{2} + c_{55} - C}$$

$$v_{p}(qP) = (2\rho)^{-1/2} \sqrt{c_{11}l_{1}^{2} + c_{33}l_{3}^{2} + c_{55} + C}$$

$$C = \sqrt{[(c_{11} - c_{55})l_{1}^{2} + (c_{55} - c_{33})l_{2}^{2}]^{2} + 4[(c_{13} + c_{55})l_{1}l_{3}]^{2}}$$
(76)

are the phase velocities and

ı

$$\Gamma_{11} = c_{11}l_1^2 + c_{55}l_3^2 \Gamma_{33} = c_{55}l_1^2 + c_{33}l_3^2$$
(77)

are components of the Kelvin-Christoffel matrix. We have omitted the bars over the elasticity constants for simplicity. The wavefront is equal to the energy velocities multiplied by one unit of propagation time.

I AVO classes of a source-rock layer

The scattering coefficients for a layer can be found in Carcione (2001a,b; 2007). For an incidence wave with subscript W = P or W=S, where P and S denote compressional and shear waves, the reflection-transmission coefficient vector is

$$[R_{WP}, R_{WS}, T_{WP}, T_{WS}]^{\top} = (\mathbf{B}\mathbf{A}_2 - \mathbf{A}_1)^{-1} \mathbf{i}_W,$$
(78)

where \mathbf{A}_1 and \mathbf{A}_2 are the propagator matrices related to the upper and lower media, \mathbf{B} is the propagator matrix of the layer, and \mathbf{i}_W is the incidence vector. The explicit expressions can be found in Carcione (2007) (Chapter 6).

The AVO intercept A is obtained as $\operatorname{Re}(R_{PP})$ at $\theta = 0$, where where θ is the angle of incidence. We compute the AVO gradient B based on Shuey's two-term approximation $R(\theta) = A + B \sin^2 \theta$ (e.g., Carcione, 2001a). The AVO classes are identified in a crossplot of gradient and intercept.

J List of symbols

sub- and super-scripts	sm, i, m, w, k: smectite, illite, matrix, water, kerogen
sub- and super-scripts	o, g, s, f, if, p: oil, gas, solid, fluid, pore-infill, pore
E	activation energy
Α	infinite-temperature rate
R	gas constant
a, b	van der Waals parameters
API	oil API gravity
S _C	weight fraction of sodium chloride
S	sedimentation rate
G	geothermal gradient
Т	temperature
t	deposition time
z	depth
q	acceleration of gravity
s	kerogen/oil or oil/gas fraction
r	smectite/illite fraction
r_0	initial smectite fraction or gas patch radius
p_{c}	confining pressure
рн	hydrostatic pressure
p	pore pressure
$p_d = p_c - p$	differential (effective) pressure
Δp	excess pore pressure
V	volume
A, B	Krief parameters (or intercept and gradient)
K.	bulk modulus
μ_{-}	shear modulus
λ, μ	Lamé constants
ρ	shale density
Ŷ	Young modulus
ν	Poisson ratio
ρ_s	smectite-illite density
$\bar{\rho}_s$	smectite-illite-water density
v_P, v_S	P- and S-wave velocities
θ	phase angle (propagation direction) or incidence plane-wave angle
v_p, v_e	phase and energy velocities
c_{IJ}	elasticity constants of the single constituents
\bar{c}_{IJ}	elasticity constants of the shale
ϵ, δ, γ	anisotropy parameters
v_{IJ}	wave velocities
I_P, I_S	P- and S-wave impedances
ϕ .	proportions
$\phi_{OC} = \phi_k + \phi_o + \phi_g$	organic content
$\phi = \phi_w + \phi_o + \phi_g$	porosity
$\mathbf{K} = 100 \ \phi_k$	kerogen content (volume percent)
TOC	Total organic content (weight percent)
$S_{\cdot} S'_{\cdot}, s_{\cdot}$	saturations
R_{WX}, T_{WX}	reflection and transmission coefficients
	•

K Tables

Table 1. Material Properties.

Medium	Depth	v_{11}	v_{33}	v_{55}	v_{66}	v_{13}	ρ
	(km)	$(\rm km/s)$	(g/cm^3)				
smectite	-	2.8	2.8	1.7	1.7	1.43	2.2
illite	-	5	4.5	2.9	3.15	1.96	2.9
kerogen*	2	2.327	2.327	1.5	1.5	0.96	1.2
"	3	2.236	2.236	1.44	1.44	0.92	1.3
water	2	1.66	1.66	0	0	1.66	1.04
"	3	1.65	1.65	0	0	1.65	1.02
smectite-illite-water	2	3.84	2.88	1.68	2.38	1.48	2.38
smectite-illite-water	3	4.73	3.80	2.37	2.97	1.72	2.75
oil	3	1.11	1.11	0	0	1.11	0.73
gas	3	0.82	0.82	0	0	0.82	0.14

(*) K_k = 2.9 GPa and μ_k = 2.7 GPa (Mavko et al., 2009).

Table 2. Coefficients for water-properties calculation.

$w_{00} = 1402.85$	$w_{02} = 3.437 \times 10^{-3}$
$w_{10} = 4.871$	$w_{12} = 1.739 \times 10^{-4}$
$w_{20} = -0.04783$	$w_{22} = -2.135 \times 10^{-6}$
$w_{30} = 1.487 \times 10^{-4}$	$w_{32} = -1.455 \times 10^{-8}$
$w_{40} = -\ 2.197 \times 10^{-7}$	$w_{42} = 5.230 \times 10^{-11}$
$w_{01} = 1.524$	$w_{03} = -1.197 \times 10^{-5}$
$w_{11} = -0.0111$	$w_{13} = -1.628 \times 10^{-6}$
$w_{21} = 2.747 \times 10^{-4}$	$w_{23} = 1.237 \times 10^{-8}$
$w_{31} = -6.503 \times 10^{-7}$	$w_{33} = 1.327 \times 10^{-10}$
$w_{41} = 7.987 \times 10^{-10}$	$w_{43} = -4.614 \times 10^{-13}$

Table 3. Kimmeridge-shale velocities at 2146 m depth. (Vernik, 1995)

p_c	v_{11}	$v_{\rm P}(45)$	v_{33}	v_{55}	v_{66}
(MPa)	$(\rm km/s)$	$(\rm km/s)$	$(\rm km/s)$	$(\rm km/s)$	$(\rm km/s)$
10	3.13	2.89	2.8	1.33	1.62
20	3.37	3.23	3.01	1.52	1.8
30	3.49	3.26	3.17	1.63	1.89
50	3.68	3.40	3.34	1.74	2.02
70	3.76	3.48	3.42	1.80	2.07

p_c	$v_P(0)$	$v_P(45)$	$v_P(90)$	$v_S(0)$	$v_{S}(90)$
(MPa)	(m/s)	(m/s)	(m/s)	(m/s)	(m/s)
5	2690	2890	3520	1490	1910
30	2820	3030	3680	1540	1990
70	2920	3150	3790	1570	2020
p_c	\bar{c}_{11}	\bar{c}_{33}	\bar{c}_{13}	\bar{c}_{55}	\bar{c}_{66}
(MPa)	(GPa)	(GPa)	(GPa)	(GPa)	(GPa)
5	23.1	13.5	3.1	4.1	6.8
30	25.2	14.8	3.8	4.4	7.4
70	26.8	15.9	5	4.6	7.6
p_c	c_{11}^{m}	c_{33}^{m}	c_{13}^{m}	c_{55}^{m}	c_{66}^{m}
(MPa)	(GPa)	(GPa)	(GPa)	(GPa)	(GPa)
5	19.2	2.3	4.8	3.3	6.5
30	19.6	13.1	5.3	4	6.8
70	19.7	15.8	5.5	4.3	6.9

Table 4. Kimmeridge-shale properties at 2768 m depth.

Table 5. Intercept and gradient of a source-rock layer.

$S_a = S'_a = \mathbf{K}(\%)$	
$\approx g \qquad \approx g = (, \circ) =$	A = B
0 0 25 -0	.24 0.42
0.1 0.02 24.4 -0	.25 0.44
0.2 0.05 23.7 -0	.26 0.48
0.3 0.08 22.8 -0	.27 0.49
0.4 0.13 21.6 -0	.29 0.51
0.5 0.2 20 -0	.32 0.52
0.6 0.3 17.5 -0	.35 0.54
0.7 0.46 13.3 -0	0.4 0.55
0.8 0.8 5 -0	.48 0.56

L Figures



Fig. 1 Organic shale components indicating the "porosity" corresponding to the Backus and Gassmann models. The porosity in the case of the Gassmann model includes the solid pore infill. The actual porosity, ϕ , of the rock to calculate the fluid saturations is that indicated for the Backus model, i.e., the sum of the water, oil and gas proportions. The organic content porosity, $\phi_{\rm OC}$, is the sum of the kerogen, oil and gas proportions.



Fig. 2 Schematic fabric topology of transversely isotropic kerogen-rich shales, according to Backus model (a), modified Backus model (b) and Gassmann model (c). The z-direction corresponds to the symmetry axis.



Fig. 3 Kerogen/oil and oil/gas fractions as a function of depth (a) and pore pressure generated due to the kerogen/oil conversion (b) ($\phi' = 0.3$ in equation (22) is assumed).



Fig. 4 Illite/smectite ratio as a function of depth.



Fig. 5 Phase-velocity variations $(v_{33} (P \text{ wave}) \text{ and } v_{55} (S \text{ wave}))$ (a) and mass density (b) of the mineral composing the shale frame as a function of depth due to diagenesis (smectite/illite conversion).



Fig. 6 TOC (in weight percent) and kerogen content K (in volume percent) corresponding to wells 1 and 3.



Fig. 7 Porosity (a) and bulk density (b) as a function of depth corresponding to wells 1 and 3. The open circles correspond to calculations performed with the properties given in Table 1.

42



Fig. 8 TOC (in weight percent) from well reports (solid line) and predicted by equation (9) (full circles), corresponding to wells 1 and 3.



Fig. 9 Backus (a) and Gassmann (b) bedding-normal P-wave velocities as a function of depth, corresponding to wells 1 and 3. The solid lines and open circles correspond to the well-log data and model calculations at the depths indicated at the well reports, respectively.



Fig. 10 Bedding-normal S-wave velocity as a function of depth, corresponding to Backus averaging (a) and Gassmann equation (b). The solid lines and open circles correspond to the well-log data and model calculations at the depths indicated at the well reports, respectively.



Fig. 11 Anisotropy parameters as a function of depth obtained from the Backus (a) and Gassmann (b) models, corresponding to wells 1 and 3, at the depths where TOC is given in the well reports.



Fig. 12 Sonic, density and Gamma ray logs.



Fig. 13 Bulk density from logs (a) and theory (b), corresponding to an smectite/illite activation energy of 39 kcal/mol and a smectite density of 2.2 g/cm³.



Fig. 14 Bedding-normal P-wave velocity from logs (a) and theory (b), corresponding to an smectite/illite activation energy of 44 kcal/mol and a smectite density of 2.6 g/cm³.



Fig. 15 Density (a) and bulk modulus (b) of the fluids as a function of depth.



Fig. 16 Effective bulk modulus of the oil-gas mixture as a function of frequency due to the mesoscopic-loss mechanism. The Wood average is also shown.



Fig. 17 Bedding-normal (a) and bedding-parallel (b) P-wave velocities as a function of gas saturation, S_g , for various values of the kerogen content, $K = 100\phi_k$, and oil saturation, S_o (dashed and solid lines, respectively). The model is Backus averaging and the frequency is 50 Hz.



Fig. 18 Bedding-normal (a) and bedding-parallel (b) P-wave velocities as a function of gas saturation for various values of the kerogen content and oil saturations (see Figure 15). The model is Gassmann equation and the frequency is 50 Hz.



Fig. 19 Energy velocity for a shale with full kerogen content (immature) (a) and a shale saturated with oil and gas (mature) (b). The model is Gassmann equation and the frequency is 50 Hz.



Fig. 20 v_P/v_S (v_{33}/v_{55}) as a function of the acoustic impedance (AI) for various values of the gas and oil saturations (solid and dashed lines, respectively). The models are Backus averaging (a) and Gassmann equation (b) and the frequency is 50 Hz.



Fig. 21 λ - μ - ρ templates for various values of the gas and oil saturations (solid and dashed lines, respectively). The models are Backus averaging (a) and Gassmann equation (b) and the frequency is 50 Hz.



Fig. 22 $Y \cdot \nu$ (Young modulus-Poisson ratio) templates for various values of the gas and oil saturations (solid and dashed lines, respectively) and three definitions of the Poisson ratio (a,b and c). The model is Backus averaging.



Fig. 23 Wet-rock wave velocities as a function of pressure corresponding to experimental data for the Kimmeridge shale (Vernik, 1995) (a) and to the present model (b).



Fig. 24 Dry-rock velocities (dashed lines) and wet-rock velocities (solid lines) as a function of the differential pressure for full kerogen (a) and $S_o = 0.3$ and $S_g = 0.1$ (b).



Fig. 25 v_P/v_S (v_{33}/v_{55}) as a function of the acoustic impedance (AI) (a) and λ - μ - ρ template for different values of the pore pressure and varying oil saturation. The model is Gassmann equation and the frequency is 50 Hz.



Fig. 26 Source-rock layer to study the AVO effects of organic matter.



Fig. 27 Real part of the reflection and transmission coefficients at depths of 2 km (a) and 3 km (b), corresponding to a source-rock layer of h = 15 m (thickness) and gas saturation $S_g = 0.2$. The model is Gassmann equation and the frequency is 30 Hz.



Fig. 28 Intercept gradient plot corresponding to a source-rock layer of h = 25 m thickness and varying gas saturation S'_g . The model is Gassmann equation and the frequency is 30 Hz.