ELASTIC, MICROSTRUCTURAL AND GEOCHEMICAL CHARACTERIZATION OF KEROGEN MATURITY FOR SHALES

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the Faculty of the Department of Earth and Atmospheric Sciences

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In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

By

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ELASTIC, MICROSTRUCTURAL, AND GEOCHEMICAL CHARACTERIZATION OF KEROGEN MATURITY FOR SHALES

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ABSTRACT

This dissertation focuses on how the kerogen content and its maturity affect the seismic properties for organic-rich shale reservoirs. The dissertation links geochemistry, seismic and petrophysics.

The experimental part of the dissertation involves rock-eval pyrolysis, TOC estimation, and anhydrous pyrolysis for artificial maturation, kerogen isolation, porosity and ultrasonic measurements on shales and kerogen. It also involves working with SEM and micro-CT scan for microstructural characterization. Porosity and seismic velocities are measured on an immature Green River shale sample. The sample is then subjected to anhydrous pyrolysis for artificial maturation by cooking the sample at 350° C for three days. Hydrocarbon induced cracks are visible on the sample. A weight loss of 9 grams is observed after maturation. The matured sample is compacted, reshaped and ultrasonic measurements are repeated. A significant change in the P-wave anisotropy (ϵ) is observed after maturation, all of which indicates that hydrocarbon induced cracks have no significant effect on seismic velocities. The ultrasonic velocities of isolated Kerogen are also measured. The measurements are carried out on the immature (Green River shale) and matured (Irati shale) kerogen samples. The bulk modulus of kerogen is found to be between 4-5 GPa.

The theoretical part of this dissertation involves kerogen maturity modeling, as well as micro structural characterization using GSA. Kerogen maturity modeling is carried out on Bakken shale published data. Hydrocarbons that are generated during maturation develop over pressure. Immature source rocks are under the normal pressure regime and mature source rocks are under the overpressure regime. The properties of matured shale are expressed in terms of excess pore pressure. P and S wave velocities decrease and anisotropy increases with the rise of kerogen maturity. The wave propagation of elastic waves (especially P and Sv waves) is affected by kerogen maturity. Maturity also affects AVO (Amplitude Variation with Offset). GSA method is used for microstructural characterization of Green River shale samples. One of the major advantages of GSA over other methods is that we can estimate the connectivity between pores/cracks (friability). The inversion results show that the pores have spherical shape and are well connected.

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Chapter 1

Introduction

1.1 Motivation and Objectives

Successful exploration and production programs for organic-rich shales depend mainly on the kerogen characterization, i.e., identification of kerogen content and its maturity through indirect seismic methods. The major difference between a conventional reservoir and an unconventional reservoir is the addition of organic matter in the unconventionals. Organic matter consists of kerogen (~90%) and bitumen (~10%). When the kerogen matures, it initially produces oil, and then gas. There is still some residue leftover in the form pure carbon (graphite) as shown in the Figure 1.1. The seismic properties of kerogen remain poorly understood, with the result that predicting the seismic response of kerogen rich rocks and kerogen maturity is a real challenge. To better understand the hydrocarbon production from shales, a multi-disciplinary approach between geology, geomechanics, geochemistry, geophysics, petrophysics, and rock physics play an important role (e.g., Bohacs et al., 2005; Vanorio et al., 2008; Prasad et al., 2009).

The objectives of this project are to link the geochemistry, rock physics and geophysics for successful characterization of shale plays. The main goals of the research are to understand how the kerogen maturation affects the seismic (velocities and anisotropy), petrophysical (porosity, bulk density and grain density), microstructural and geochemical properties (TOC and hydrogen index).



Figure 1.1: Generation of hydrocarbons from kerogen maturation (modified after Passey et al., 2010)

1.2 Controls on organic carbon richness

Phytoplankton (Phyto=plant; plankton=floating; e.g. algae) are the primary producers of the organic carbon. They use sunlight to convert inorganic carbon to organic carbon through photosynthesis (Figure 1.2). Zooplankton (Zoo=animal) eat phytoplankton and these are consumed by big animals in the ocean. Only a small fraction (approximately 0.1%) of the organic matter that sinks to the ocean floor is subsequently

buried in the seafloor and incorporated into marine sediments and sedimentary rocks (Falkowski and Oliver, 2007). Oxygen in the water column supports biologic productivity of organic matter, but it also supports biodegradation and oxidation, which reduce the organic richness. The accumulation of organic matter is controlled by three variables: production, destruction and dilution. The mathematical expression of these variables is (Bohacs et al., 2005; Passey et al., 2010):

Organic-matter enrichment = Production - (Destruction + Dilution), where

Production = *f*(Nutrient supply),

Destruction = f(Production of organic matter) + f(Oxidant exposure time) - f(Clastic sedimentation rate < burial-efficiency threshold),

Dilution = f(Clastic sedimentation rate > burial-efficiency threshold) + f(Production of biogenic silica or carbonate).

A significant amount of organic enrichment occurs where organic-matter production is maximized, destruction is minimized, and dilution by clastic or biogenic material is optimized.



Figure 1.2: Schematic showing burial of organic carbon with marine sediments (After Falkowski and Oliver, 2007)

Kerogen (kero means "wax" and –gen means "that which produces" in Greek) (Oxford dictionary, 2003) is a mixture of organic chemical compounds that make up a portion of the organic matter in sedimentary rocks. Kerogen is normally defined as that portion of the organic matter present in sedimentary rocks that is insoluble in ordinary organic solvents. Each kerogen molecule is unique and possesses complex structure formed by the random combination of many small molecular fragments. The chemical and physical characteristics of a kerogen are strongly influenced by the type of biogenic molecules from which the kerogen is formed, as well as by the diagenetic transformations of those organic molecules.

Kerogen does not have a concrete structure, as it is a mixture of organic materials of a chemical compound and its chemical composition can vary from sample to sample.

For example, kerogen from the Green River formation oil shale deposit of western North America this study) contains elements following (used in in the carbon 215 : hydrogen 330 : oxygen12 : nitrogen 5 : sulfur 1 proportions; (Yen and Chilingar, 1976). Kerogen composition is also affected by thermal maturation processes (like catagenesis and metagenesis) that alter the original kerogen. As the subsurface heats up over geological time, the kerogen breaks into lighter hydrocarbons and produces oil and gas. The residual kerogen also undergoes important changes, which are reflected in their chemical and physical properties.

The term kerogen was originally coined to describe the organic matter in shales that yielded oil upon retorting. Kerogen is known as dispersed organic matter in sedimentary rocks. The amount of organic matter tied up in the form of kerogen in sediment is far greater than that in living organisms or in economically exploitable accumulations of coal, oil, and natural gas.

1.2.1 Geological elements and processes

Kerogen deposition and its maturation occur over millions of years in a sedimentary basin. For example, if the organic matter is deposited along with fine grained sedimentary rock during the Paleozoic era in a basin (Figure 1.3), and over burden sedimentation and compaction take place continuously. Due to temperature and pressure, hydrocarbon generation and expulsion occur during the Jurassic era. The leftover organic matter undergoes thermal maturation over time, from the Jurassic era to the present, as a continuous process.

300		Ge	ologica 200	1 Time (N	la) 		Events of source rock Petroleum system	
Pale	ozoic		Mes	ozoic	Cene	ozoic		
С	Per	Tr	J	к	Pg	Ng		
							Fine grained rock + Organic Matter	ents
		Over burden sedimentation	Elem					
							Hydrocarbon generation	sess
							Migration and leftover OM	Proce

Figure 1.3: Elements and processes for organic matter deposition and maturation in a sedimentary basin

1.2.2 Kerogen composition

Researchers at the IFP (Institute of French Petroleum) have developed a scheme to describe different types of kerogen (Behar and Vandenbroucke, 1987). They have identified three main types of kerogen (called Types I, II, and III) and have studied the chemical characteristics and the nature of the organisms from which all types of kerogens were derived. Subsequent investigations have identified Type IV kerogen as well. Table 1.1 shows types of kerogen with examples.

Type I kerogen is derived principally from lacustrine algae. The best-known example is the Green River shale, of the middle Eocene age, from Wyoming, Utah, and Colorado in the USA. Type I kerogen have high generative capacities for liquid hydrocarbons. Irati shale used for my research is also a type I kerogen. Type II kerogen arises from several very different sources, including marine algae, pollen and spores, leaf waxes, and fossil resin. They also include contributions from bacterialcell lipids. Type II kerogen generate either liquid hydrocarbons or gas. Most Type II kerogens are found in marine sediments deposited under anoxic conditions. Type II kerogen containing high Sulfur content is known as type II-S kerogen. Monterey formation in California is an example for type II-S kerogen.

Kerogen	Source material	Environment of	HC	Example
Туре		Deposition	prone	
Ι	Mainly algae	Lacustrine	Oil	Green River and
				Irati shales
II	Mainly plankton,	Marine	Oil/gas	Kimmeridge shale
	also algae			
II-S	Mainly plankton,	Marine	Oil/gas	Monterey from
	also algae			СА
III	Terrigenous plant	Shallow to deep	Dry gas	Mostly coals
		marine		(CBM?)
IV	Residual Organic	Reworked	No	
	matter		potential	

Table 1.1: Different types of kerogen with examples (www.spec2000.net).

Type III kerogens are composed of terrestrial organic material. Cellulose and lignin are major contributors. Type III kerogens have much lower hydrocarbongenerative capacities than do Type II kerogens and, unless they have small inclusions of Type II material, are normally considered to generate mainly gas. Type IV kerogens contain mainly reworked organic debris and highly oxidized material of various origins. They are generally considered to have essentially no hydrocarbon-source potential.

Kerogen sulfur, in contrast, is derived mainly from sulfate that was reduced by anaerobic bacteria. High-sulfur kerogens (and coals) are almost always associated with marine deposition, because fresh waters are usually low in sulfate. Sulfur is only incorporated into kerogens in large quantities where sulfate reduction is extensive and where Fe⁺² ions are absent (organic-rich, anoxic, marine, nonclastic sediments). Many high-sulfur kerogens are also high in nitrogen. The different types of kerogen particles are called macerals. Macerals are essentially organic minerals; they are similar to what minerals are to a rock.

1.2.3 Kerogen maturation

Kerogen maturation occurs when a kerogen is subjected to high temperatures over long periods of time. Thermal maturation transforms solid kerogen into liquid oil and gas. Thermal decomposition reactions, called catagenesis and metagenesis (Figure 1.4), break off small molecules and leave behind a more resistant kerogen residue. The small molecules eventually become petroleum and natural gas. By convention the term catagenesis usually refers to the stages of kerogen decomposition during which oil and wet gas are produced. Metagenesis, which occurs after catagenesis, represents dry-gas generation.

Although the terms catagenesis and oil generation are often used synonymously, they are not precisely equivalent. Catagenesis and hydrocarbon generation occur concurrently, but they represent different aspects of the same process. Catagenesis

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involves the transformation of kerogen molecules, whereas hydrocarbon generation focuses on the production of hydrocarbon molecules.

Kerogen maturation is not a reversible process, and the chemical process of maturation never stops completely, even if drastic decreases in temperature occur. Chemical reaction-rate theory mandates that the rates of reactions decrease as temperature decreases; however, it also states that, at any temperature above absolute zero reactions will occur at some definable rate. For practical purposes, however, the rates of catagenesis are generally not considered important at temperatures below about 70° C. If the temperature decreases to about 20°-30° C due to subsurface events, erosional removal will cause the rates of catagenesis to decrease so much that they become negligible for practical purposes.



Figure 1.4: Schematic showing the production of hydrocarbons with the increase of temperature (Courtesy from Crains petrophysics handbook).

It is impossible to set precise and universal temperature limits for catagenesis, as time also plays a role. Old rocks will often generate hydrocarbons at significantly lower temperatures than young rocks, simply because the longer length of time compensates compensates for lower temperatures. Catagenesis starts at around 60° C and reaches upto 225° C. It produces both oil and wet gas.

Nitrogen and sulfur are also lost from kerogens during catagenesis. Nitrogen loss occurs primarily during late catagenesis or metagenesis, after hydrogen loss is well advanced. In contrast, much of the sulfur is lost in the earliest stages of catagenesis, as evidenced by low maturity, high-sulfur oils found in a number of areas, including the Miocene Monterey formation of southern California.

Kerogen particles become darker during catagenesis and metagenesis, much as a cookie browns during baking. There is a steady color progression yellow-goldenorangelight brown-dark brown-black as a result of polymerization and aromatization reactions. These reactions are intimately related to important changes in the chemical structure of kerogen, but they are not necessarily identical with hydrocarbon generation. There is therefore no necessary cause-and-effect relationship between kerogen darkening and hydrocarbon generation, and no guarantee that a particular kerogen color always implies the onset of oil generation. As kerogen matures and becomes more aromatic, its structure becomes more ordered, since the flat aromatic sheets can stack neatly (Figure 1.5). These structural reorganizations bring about changes in physical properties of kerogens. One property that is strongly affected, and which can be used to gauge the extent of molecular reorganization, is the ability of kerogen particles to reflect incident light coherently. The more random a kerogen's structure, the more an incident light beam will be scattered, and the less it will be reflected.

Some properties of kerogen change very little during catagenesis. For example, carbon-isotopic compositions of kerogens are little affected by maturation. Except for darkening, the visual appearance of kerogen also does not change during catagenesis:

kerogen types are generally recognizable until the particles become black and opaque, somewhat beyond the oil-generation window.



Figure 1.5: Changes in the kerogen structure with maturation (a) At the beginning of diagenesis (b) At the beginning of catagenesis (c) At the end of catagenesis. (Modified after Behar and Vandenbroucke, 1987).

Effective generation of hydrocarbons requires that the generated products be expelled from the source-rock matrix and migrated to a trap. Timing and efficiency of expulsion depend on a number of factors, including rock physics and organicgeochemical considerations. Many workers now believe that microfracturing of source rocks is very important for hydrocarbon expulsion. Microfracturing is related to overpressuring, which in turn is partly attributed to hydrocarbon generation itself. Rich rocks will become overpressured earlier than lean ones and thus will also expel hydrocarbons earlier. In very lean rocks expulsion may occur so late that cracking of the generated bitumen is competitive with expulsion. In such cases the expelled products will be mainly gas.

1.3 Review of published literature

Micro-structural characteristics of organic rich shale can provide important insights into the maturation processes and oil generation from such formations (Vernik and Nur, 1992). Attempts have been made to relate acoustic velocity and velocity anisotropy to the degree of kerogen maturity of the shales (Vernik and Nur, 1992; Vernik and Liu, 1997). Prasad et al (2009, 2011) attempted to establish a relation between elastic properties and kerogen microstructure and changes in elastic properties during maturation. They have used scanning acoustic microscopy to map the impedance microstructure of kerogen-rich shales (Figure 1.6). Zargari et al. (2011) have observed the microstructural changes of kerogen before and after pyrolysis (Figure 1.7). Elbaharia and Batzle (2011) have measured the elastic properties of Green River shale in an apparatus and the plot between velocities and temperature is shown in the Figure 1.8. Vernik and Milovac (2011) show that the main controls on the elastic properties of organic shales consist of the following: kerogen content, porosity, clay content, and effective stress. The high level of velocity anisotropy observed in organic shales is shown to be related to the lenticular distribution of kerogen and the preferred orientation of clay minerals parallel to the bedding plane. Kobchenko et al. (2011) observed that additional horizontal cracks are created within the kerogen after heating the immature shale sample (Figure 1.9). Zhu et al. (2011) used numerical modeling to predict mudstone physical properties and seismic responses. They showed the physical relationships between seismic properties such as (P-wave impedance and Vp/Vs) and shale rock properties such as mineralogy, TOC, and porosity.



Figure 1.6: Impedance microstructure in the Bakken Formation. The numbers show the Hydrogen Index HI (upper right corner) in each shale sample. A decreasing HI number denotes increasing maturity. The color code (0–100% grey shade) varies from high (100% = 50 km/s*g/cm3) to low (0% = < 7 km/s*g/cm3) impedance. The lowest impedance is red. Note change in texture (decrease in red color) from immature (HI = 319) to mature shales (HI = 122). The images scale in (a) is $1x1mm^2$ and the image scale in (b) is 62 x 62 µm². From Prasad et al. (2009).

Figure 1.7: Comparing the shale sample before pyrolysis (a) and after pyrolysis (b). Observe the changes in the kerogen (red arrows). From Zargari et al. (2011).

Figure 1.8: Plot between velocities (Vp and Vs) with temperature. The sample cut parallel to bedding and has TOC of 27.5%. From El Baharia and Batzle (2011).

Lucier et al. (2011) have examined the effects of different parameters, such as lithology, porosity, TOC, and water saturation on a P-wave velocity, as well as the Vp/Vs ratio from a well in the Bossier/Haynesville shale gas play. They have found that the fluid saturation effect predicted by Gassmann's equation plays a major role in velocities, which show a consistency with mud line velocity (Castagna et al, 1993). Clearly, our knowledge of the effects of the TOC and its maturation on velocities dispersed.

Based on studies carried out for the past two decades, a link between laboratory studies and seismic properties of the effect of kerogen is still missing and clearly, the critical factors for seismic characterization of organic rich shale's are not fully understood.. Additionally, not much detailed analysis has been conducted conerning the effect of velocities on kerogen maturation. Nor have seismic models of before and after maturation been built. The hope is that this proposed work plan will yield a better understanding of seismic wave propagation and the amplitude changes caused by kerogen content and maturation.

Figure 1.9: Thin section images of Green River Shale sample before and after heating. (a) Interlaminated silt and clay-rich layers before heating. Here f indicates clay-rich layers with a higher amount of kerogen lenses and c indicates coarser layers with siliciclastic grains. (b) Detail of a kerogen lens. (c) Image of the same sample after heating. Arrows indicate the position of cracks developed during heating. Fractures propagated mainly in the finer grained intervals where the highest concentration of organic matter lenses was also observed. (d) Detail of a crack filled with organic remains (arrows). From Kobchenko et al. (2011).

Kanitpanyacharoen et al. (2013) have heated Kimmeridgian shale samples at elevated temperatures and observed that a significant amount of air bubble formation occurs at around 400° C. They also observed kerogen shrinkage and clay matrix expansion when the samples are heated upto 500° C for 10 hours.

Figure 1.10: SEM images of same location of Kimmeridge shale heated at different temperatures (Kanitpanyacharoen et al., 2013)

1.4 TOC in shales

The level of TOC (Total Organic Carbon) in shales contributes to the production of oil and gas after maturation. However, the conversion of TOC to hydrocarbons depends on the origin of organic material (Jarvie et al., 2007). TOC contains live (convertible) carbon and dead (inert) carbon. The hydrocarbon potential of live carbon
depends on the amount of hydrogen present, which depends on the type of the organic matter. For a type I/II kerogen, where the origin is mainly algae or plankton, the majority of the live carbon converts to oil/gas upon thermal maturation. A small portion of dead carbon remains present in the live carbon (Figure 1.11a). A minor amount of dry gas is produced after over maturation from dead carbon. The hydrocarbon generative potential for a type III kerogen, where the origin is land-derived woody material, is less when compared with type I/II kerogen upon maturation. The live carbon part of type III converts to dry gas after over-maturation (Figure 1.11b). Coal bed methane (CBM) is an example for type III. Alginites (type I/II) contain more hydrogen than vitrinites (type III); consequently, we can expect a greater pore volume yield from the decomposition of alginites (Loucks et al., 2009).



Figure 1.11: Schematic showing the conversion of TOC for (a) type I/II kerogen and (b) type III kerogen

1.5 Porosity development in shales

Three different types of pores have been identified in shales (Loucks et al., 2012; Milliken et al., 2013). Two pore types are associated in the non-organic mineral matrix (interparticle and intraparticle pores) and intraparticle pores are associated with the organic matter. During the initial stages of deposition, clay platelets, silt/calcite grains and organic matter are deposited on the ocean floor. It will have very high porosity. After compaction due to overburden sedimentation, the porosity is reduced. The grain to grain contact increases. Ductile clay platelets are overlain on the rigid silt grains and develops inter-particle porosity (Figure 1.12).



Figure 1.12: Schematic showing the pore generation in organic shales

With the increase of compaction, inter-particle (between the grains) pores are formed. As the temperature increases (maturation), intra-particle pores develop in the organic matter. Intra-particle pores also develop within the non-organic part of the shales due to chemical reactions (Figure 1.12)

1.6 Hydrocarbon production from nano pores

It is always a challenge for the geoscientists and engineers to understand how the low permeable, nano porous shales produce gas or oil. Passey et al. (2012, 2010) have tried to explain the gas production derived from the shales. Though the organic matter has pores of nano meter size, it can still hold methane (size~0.4 nm) molecules in the form of both adsorbed and free gas. In Figure 1.13, the red dots are adsorbed methane, and the shaded red color indicates either free gas or solution gas (gas dissolved in liquid). The blue lines indicate the distribution of water.



Figure 1.13: Hypothetical distribution of gas and water in organic matter (Passey et al., 2010).

If a bigger pore (~40 nm) exists, it means that the presence of free gas is more than the adsorbed gas. If a small pore exists (~2 nm), it means that the adsorbed gas dominates the pore. Therefore, the adsorbed gas fraction is higher in small organic matter pores.

The intra-particle pores in the organic matter look like isolated, disconnected pores on the 2D SEM images. However, these pores are connected in the 3D reconstructed SEM images (Figure 1.14a). With the help of digital rock physics, one can identify connected and isolated pores within the organic matter (Figure 1.14b).



Figure 1.14: (a) 3D reconstruction of 2D SEM images (b) Connected and isolated in the organic matter (Walls and Sinclair, 2011).

1.7 Proposed research plan

The proposed plan is the following: collect an organic rich immature shale sample; measure the ultrasonic velocities, porosity, microstructure with SEM, micro CT scan. Isolate the kerogen of the same immature shale; measure the elastic properties of this immature kerogen. Carry out anhydrous pyrolysis on the immature sample and repeat the above measurements and finally destruct it to get the kerogen. Measure elastic properties on the mature kerogen. Finally, one can form an idea about how the kerogen maturation is affecting the elastic properties.

1.8 Data available

- Immature Green River shale plugs (Three horizontal plugs with different TOC) from Colorado, US
- Irati shale plugs (Two vertical plugs with different TOC and maturity) from Brazil.
- Post-stack seismic data with well logs of Barnett shale from the Fort Worth basin, US.
- 4. Published data on ultrasonic measurements on immature Bakken shale from the Williston basin, for numerical modeling of maturity.
- 5. Published literature on different shales around the world.

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Chapter 2

Geochemical and microstructural characterization

2.1 Abstract

This chapter summarizes the geochemical and micro-structural characterization carried out on Green River and Irati shale plugs. Green River shales are collected from outcrops of Colorado, while Irati shales are collected from outcrops from Brazil. Rock-eval pyrolysis and TOC measurements are conducted on the shale samples. An immature organic-rich (16% TOC) Green River shale plug is subjected to anhydrous pyrolysis. The sample is heated at 350^o C for three days. Oil produced during cooking is collected. Hydrocarbon induced cracks are observed on the cooked sample. A significant amount of kerogen is transformed to oil/gas during maturation.

Micro-structural characterization of the shales is carried out using SEM and micro-CT scan. It is shown from this analysis how the hydrocarbon induced cracks are connected in three dimensional spaces on the matured sample.

2.2 Data collection

2.2.1 Irati shale

Irati shale core plugs are provided by Petrobras from Brazil. This formation is wide spread in the southern parts of Brazil. The Irati formation typically consists of two

oil shale beds. The upper layer is thicker (30 ft) than the thinner lower bed (10 ft). But the lower bed has more potential than the upper bed. The lower bed has around 12% of oil yield, while the upper layer has around 7% oil yield. The oil shale yield varies laterally, and may be as little as 7% for the lower layer and 4% for the upper layer. The formation is a very fine grained and laminated deposit. The color of the Irati shale varies from dark gray to brown to black. Around 60-70% of Irati shale consists of clay minerals and the rest is composed of organic matter. According to Padula (1969), the strata of the Irati formation can be classified into two distinct facies: (1) dark-gray and brown to black oil shale and light to dark-gray non bituminous shale which contains little organic matter and yields no oil, and (2) cream to dark-gray limestone and dolomite. The organic matter does not dissolve in organic solvents. When the Irati shale formation is heated, it produces vapors of bitumen and sulfur. The average mineralogical composition from thin section analysis (Padula, 1969) is mica and clay minerals (60-70%); organic matter (20-30%); quartz or calcite (1-10%). Density of the Irati formation ranges from 1.8 to 2.45 g/cc and the shale contains 2 to 14% oil (Bruni et al., 2000). Bulk density of Irati shale decreases with the increase of organic matter.

2.2.2 Depositional environment

Various researchers have proposed different hypotheses for the depositional environment for Irati shale. However, the most widely accepted theory (e.g., Beurlen, 1955; DaSilva and Cornford, 1985) suggests that the organic material in the Irati oil shale originates from algae deposited in a lacustrine environment with salinity varying from that of freshwater to brackish water. Subsequently, the fine grained clastic material brought in by rivers formed the carbonate rocks and shale of the Irati formation.

2.2.3 Oil mining

The Brazilian national oil company (Petrobras) started oil shale extraction technology (Petrosix) in 1991. First, oil shale is extracted from the mine (Figure 2.1a) and then it is subjected to the Petrosix process. This process involves heating oil shale to a high temperature through injecting hot gas into the chamber (Figure 2.1b). Petrobras extracts around 3800 bbl of oil every day by using this technology (Martignoni and Rotriguez, 2010).





RPL received four core plugs of the Irati shale from Petrobras. One out of the four plugs is an artificially cooked sample (Irati-1 sample). Figure 2.2 shows the thin section of the cooked Irati shale. This sample (IR-1) is used for this research. Kerogen is isolated

from this sample to measure the ultrasonic velocities and bulk modulus of a matured kerogen.



Figure 2.2: Thin section of Irati shale (IR-1) sample (Image courtesy from Xioafan Hu). 2.3 Green River shale

The Green River formation contains the largest oil shale deposits in the world. It has been estimated that the oil shale reserves could be equal to up to 3 trillion barrels (480 billion cubic meters) of shale oil. We can recover up to half of these reserves by using shale oil extraction technologies (by cooking the kerogen). U.S. conventional oil reserves are only about 1/10th those of Saudi Arabia (Rapier, 2013). But, Green River shale may have more oil reserves than any other country.

2.3.1 Geological setting

Green River shale was formed during the Eocene age. It is a lacustrine type deposition. The kerogen is type-I kerogen. It spreads over three states in USA: Colorado, Wyoming and Utah. The warm conditions of the lakes provided an excellent source for organic matter generation especially blue-green algae (Dyni, 2005). Big oil companies such as Shell, ExxonMobil and Chevron have been running projects to extract the oil from the Green River formation.

The outcrop samples used in this study were acquired in Wyoming. The samples were collected from Green River basin and the location is shown in the Figure 2.3 (dashed ellipsoid).



Figure 2.3: Location of the out crop Green River shale samples

2.4 Total Organic Carbon (TOC):

Organic carbon is the remnant of ancient life preserved in sedimentary rocks. Organic carbon is formed after degradation by chemical and biological activities. This is supported by the depth of the burial, the temperature and the pressure. Total organic carbon (TOC) is an indicator of source rock quality and organic richness (Jarvie, 1991).

The organic matter in a potential source rock must be capable of generating petroleum. Recycled organic material, which has already been buried in sediments and has no potential to generate oil or gas, must be excluded from the total when defining the TOC in a rock. The amount of petroleum generated and expelled from a source rock increases as the atomic hydrogen-to-carbon (H/C) ratio of the organic matter increases (Hunt, 1996). TOC is reported in weight percent (wt. %) carbon, (e.g., 1.0 wt. % carbon means that for 100 grams of rock sample, there is one gram of organic carbon). Figure 2.4 shows the amount of burial kerogen and how much of it was converted to shale oil or oil shale (through pyrolysis) and gas (modified from Vandenbroucke and Largeau, 2007; Durand, 1980). Thermal maturity measures the degree to which a formation has been exposed to high heat that needed to break down the organic matter to hydrocarbons.



Figure 2.4: Picture showing the total amount of kerogen preserved in sedimentary rocks (Modified after Vandenbroucke and Largeau, 2007).

2.4.1 TOC measurements in the lab

TOC can be measured in the lab using the Leco combustion method (Jarvie, 1991). A method that uses about 1gr of the crushed sample. The in-organic part of the crushed sample is removed by soaking the sample in HCl for 12-16 hours. After that, the sample is rinsed free of HCl by using water, and filter paper. The Leco carbon analyzer (Figure 2.5) is calibrated using a steel standard of known carbon content. Then the sample is analyzed and oxidized to carbon dioxide, after which it is analyzed by an infrared (IR) or a thermal conductivity (TC) detector. Finally, we can measure the total organic carbon content.



Figure 2.5: Leco's TOC measurement system at the Geochemistry lab at UH. The results of the TOC for five samples (Green River shale=3; Irati shale=2) are shown in the Table 2.1.

2.5 Rock-eval pyrolysis

Rock-eval pyrolysis is used to identify the type and maturity of organic matter and to detect petroleum potential in sediments. The Rock-eval pyrolysis method consists of the programmed temperature heating (in a pyrolysis oven) in an inert atmosphere (helium) of a small sample (~100 mg) to quantitatively and selectively determine (1) the free hydrocarbons contained in it, and (2) the hydrocarbon- and oxygen-containing compounds (CO₂) that are volatilized during the cracking of the organic matter (kerogen). The set up for the rock-eval pyrolysis is shown in the Figure 2.6.



Figure 2.6: Apparatus set up for rock-eval pyrolysis at the geochemistry lab at UH.

The pyrolysis oven temperature program is as follows: for 3 min, the oven is kept isothermally at 300°C, and the free hydrocarbons are volatilized and measured as the S_1 peak. The temperature is then increased from 300° to 550°C (at 25°C/min). This is the phase of volatilization of very heavy hydrocarbons compounds (>C₄₀) as well as the cracking of nonvolatile organic matter. The hydrocarbons released from this thermal cracking are measured as the S_2 peak. The temperature at which S_2 reaches its maximum depends on the nature and maturity of the kerogen and is called T_{max} . The CO₂ issued from kerogen cracking is trapped in the 300°-390°C range. The trap is heated, and CO₂ is released and detected during the cooling of the pyrolysis oven (S_3 peak).

One arrives at the following parameters from rock-eval pyrolysis (Tissot and Welte, 1984):

 S_1 = the amount of free hydrocarbons (gas and oil) in the sample (in milligrams of hydrocarbon per gram of rock). This is produced from hydrocarbons already converted from kerogen.

 S_2 = the sum of hydrocarbons generated through the thermal cracking of nonvolatile organic matter. S_2 is an indication of the quantity of hydrocarbons that the rock has the potential to produce should burial and maturation continue.

 S_3 = the amount of CO₂ (in milligrams CO₂ per gram of rock) produced during pyrolysis of kerogen. S_3 is an indication of the amount of oxygen in the kerogen and is used to calculate the oxygen index. S_3 peak is associated with the cooling effect.

 T_{max} = the temperature at which the maximum release of hydrocarbons from cracking of kerogen occurs during pyrolysis (top of S₂ peak). T_{max} is an indication of the stage of maturation of the organic matter. T_{max} increases with the increase of level of maturity.

Figure 2.7 shows the schematic of how the peaks look like with the increase of temperature. It shows of the quantity of hydrocarbons produced from kerogen with the increase of temperature during rock-eval pyrolysis.



Figure 2.7: Schematic showing the products generated during rock-eval pyrolysis

One can calculate the hydrogen index (HI) and the oxygen index (OI) from the TOC and rock-eval pyrolysis analysis. HI = hydrogen index (HI = $[100 \times S_2]/TOC$). HI is a parameter used to characterize the origin of organic matter. HI typically ranges from 0 to 1200 in geological samples.

 $OI = oxygen index (OI = [100 x S_3]/TOC)$. OI values range from near 0 to 200.

Table 2.1 shows the TOC measured in wt%, and other geochemical parameters measured from rock-eval pyrolysis for the five shale samples. The notation GR indicates Green River shale and IR indicates Irati shale.

Name	TOC	\mathbf{S}_1	S_2	S ₃	Tmax	Hydrogen	Oxygen
	(wt%)	(mg/g)	(mg/g)	(mg/g)	(C)	Index	Index (OI)
						(HI)	
GR-1	16	6.45	132.76	1.65	439	829.75	10.31
GR-2	11.5	1.80	65.59	1.49	437	570.34	12.95
GR-3	6.5	4.33	99.03	1.01	438	1523.23	15.53
IR-1	13.5	1.51	15.39	0.72	449	114	5.33
IR-2	8.5	4.05	63.5	1.05	422	747.06	12.35

Table 2.1: Geochemical measurements for Green River and Irati shales

2.5.1 Van Krevelen diagram

Modified Van Krevelen diagram plot atomic HI versus OI (Figure 2.8). This is the best method for evaluating the quality and maturation state of the source rock in the subsurface (Hunt, 1996). This method utilizes rock-eval parameters and TOC measurements. The four kerogen types mature along different evolutionary paths with the arrows pointing towards higher maturation states.



Figure 2.8: Modified Van Krevelen diagram for (a) Green River and (b) Irati shales.

From the Figure 2.8, it is evident that both GR and IR shales are type-I and all of them are in immature stage except IR-1 which is artificially matured. Figure 2.9 shows the relation between hydrogen index (HI) and T_{max} for GR and IR shale samples. This plot also provides an idea about the current level of maturity for the shale samples. All the shale samples fit inside an immature window, except IR-1, which falls inside the matured window. T_{max} increases with the level of maturity. IR-1 has a T_{max} of 440 C.



Figure 2.9: Relationship between HI and T_{max} for (a) GR shales and (b) IR shales

2.6 Pyrolysis

Pyrolysis is the thermo-chemical decomposition of organic material at elevated temperatures in the absence of oxygen. There are two types of pyrolysis: (1) hydrous pyrolysis and (2) anhydrous pyrolysis (closed and open).

2.6.1 Hydrous pyrolysis

The processes responsible for oil generation are best simulated by hydrous pyrolysis. This technique maintains a liquid water phase in contact with organic sedimentary rocks during their heating at subcritical water temperatures (less than 375 degrees C). The expelled oil accumulates on the water surface. Hydrous pyrolysis

provides a means for acquiring information relating to stages, kinetics and indices of petroleum generation that would otherwise be difficult to obtain from only a study of the natural system (Lewan, 1985). The oil that is generated during hydrous pyrolysis accumulates on the surface of water. This oil simulates the naturally generating oil from geological maturation (Winters et al., 1983; Lewan, 1994). The major difference is that natural maturation requires millions of years, while, during pyrolysis, one can simulate the same process in the lab within a few days. Furthermore, the quantity of hydrocarbons generated is exaggerated in hydrous pyrolysis. Hydrous pyrolysis consists of two reactions: (1) the decomposition of kerogen to bitumen and (2) the decomposition of bitumen into oil (Lewan, 1985).

The presence of water during pyrolysis increases the pressure due to steam formation and may provide a source of hydrogen (Lewan and Ruble, 2002). Hydrous pyrolysis may be a significant process in the creation of fossil fuels, but it may alter the composition of oil produced during the process. Anhydrous pyrolysis, which involves heating without water has long been considered to take place naturally during the catagenesis of kerogens to fossil fuels (Comet et al., 1986). Elastic properties and moduli change after hydrous pyrolysis (e.g., Zargari et al., 2013; Elbaharia and Batzle, 2011).

Petrographic studies of rocks subjected to hydrous pyrolysis show that continuous organic networks may be established by the expansion of bitumen into the rock matrix during kerogen decomposition to bitumen (Lewan, 1987). This bitumen fills the micro pores and bedding-plane partings; the result is, the darkening of the light brown matrix of an immature rock into a dark brown matrix. This change in the matrix due to bitumen

impregnation is also observed in naturally matured source rocks suggesting that natural processes are being simulated by hydrous pyrolysis experimentation. This is most likely a net volume increase of the generated bitumen within an essentially constant-volume inorganic matrix (Lewan, 1987).

2.6.2 Anhydrous pyrolysis

Anhydrous pyrolysis involves pyrolyzing the samples in the absence of water. There are two types of anhydrous pyrolysis: (1) open and (2) closed. The difference between the types is that all the generated products will be maintained in the same thermal regime as the pyrolyzed samples (Lewan, 1994). The quantity of hydrocarbons produced in anhydrous pyrolysis is lower when compared with hydrous pyrolysis (Comet et al., 1986). Anhydrous pyrolysis provides a rapid means of characterizing organic matter and its relative hydrocarbon potential (Lewan, 1991). In the anhydrous pyrolysis experiments, the interstitial water is vaporized. Pyrobitumen is formed during anhydrous pyrolysis because of lack of water.

2.6.3 Experiment

Immature Green River shale sample (GR-1) is subjected to closed anhydrous pyrolysis at the UH geochemistry lab (Figure 2.10). This sample has higher TOC (~16% wt) and low porosity (~1%). The sample is lowered in the furnace. A detector is used to recognize any release of H₂S gas during pyrolysis. The experiment starts at atmospheric conditions, i.e. room temperature and no confining pressure. The temperature of the furnace is increased to 350 C and maintained at a constant temperature throughout the experiment for 3 days (~72 hrs). The pressure is increased to around 1000 psi at the end of the experiment (Figure 2.11). This increase in pressure is caused by the release of

hydrocarbons due to kerogen maturation. The oil generated during maturation is collected in the transfer vessel and is shown in the Figure 2.12.

The sample is taken out after the experiment. Hydrocarbon-induced cracks are observed in the sample (Figure 2.13b). These cracks result from the expulsion of hydrocarbons during maturation. They are parallel to the bedding of the sample.

Table 2.2 shows the rock properties before and after maturation. There is an approximately 14% decrease in weight and bulk density of the sample after maturation. This change is due to loss of lighter rock material (kerogen) during artificial maturation (anhydrous pyrolysis).



Figure 2.10: Anhydrous pyrolysis set up at geochemistry lab at UH



Figure 2.11: Plot showing the variations of temperature and pressure during the experiment



Figure 2.12: Picture showing oil generated during pyrolysis (oil is mixed with Di-chloro methane)



Figure 2.13: Pictures of GR-1 shale (a) before maturation and (b) after maturation

Rock Property	Before Maturation	After Maturation	% change
Length (mm)	43.7	43.7	
Diameter (mm)	36.01	36.01	
Weight (gm)	79.74	70.35	-11.77
Bulk volume (cc)	44.51	44.51	
Grain volume (cc)	44.51	44.51	
Bulk density (g/cc)	1.79	1.58	-11.73

Table 2.2: Comparison of rock properties for GR-1 before and after maturation

2.7 Kerogen isolation

Kerogen can be isolated from its rock matrix using chemical and physical means. Physical separation depends mainly upon flotation and centrifugation techniques in organic or inorganic solvents or mixtures, or on the different wettability properties of organic and inorganic matter in water and hydrocarbon solvents (Saxby, 1970). However, such methods rarely provide a complete separation (Forsman and Hunt, 1958) and usually cannot be applied to sediments containing low concentrations of kerogen. Chemical processes involve the use of strong, non-oxidizing acids and bases to dissolve the rock matrix without modifying the kerogen chemistry, morphology or color. However, not all of the minerals dissolve in chemical solvents (e.g., pyrite). One of the methods for the elimination of pyrite is by destruction, through oxidizing agents such as diluted nitric acid. The kerogen samples used for isolation (GR-1 and IR-1) do not have much sulfur (<2%). So, there is no need to apply any special chemical treatment for pyrite elimination. The main goal of kerogen isolation should be a maximum recovery and a minimal chemical reaction (Durand and Nicaise, 1980). The isolated kerogen should have the same structure as the in-situ (Goklen et al., 1984).

2.7.1 Conservative closed-system method

Figure 2.14 shows the experimental set up for kerogen isolation. The isolation process uses the conservative closed-system method (Ibrhamov and Bissada, 2010). In this process, concentrated NH_4OH is used, and the mixture is allowed to react for the desired time and removed. The reaction cells are then flushed with de-ionized water. Concentrated HF is added for the desired reaction time and then removed. Concentrated HCl is added again and removed. The cells are flushed once again with de-ionized water

before a second treatment with NH₄OH, followed by another flush with de-ionized water. In this study, these steps were repeated a number of times, depending on the mineralogy of the rocks. The dolomitic rocks required more extensive treatment with HCl, whereas the siliciclastic rocks needed more treatment with HF. At the end, the kerogen in the sealed reaction cells was treated numerous times with acidic CrCl₂ (Acholla and Orr, 1993) to dissolve pyrite. Samples high in S required at least three treatments. Finally, the kerogen was removed from the membrane filters of the reaction cells, dried in a vacuum oven. The isolated kerogen for GR-1 shale is shown in the Figure 2.15. Approximately 14 gr of GR-1 crushed shale sample were used, and approximately 3 gr of kerogen were recovered from this isolation process. The detailed automated workflow for kerogen isolation is shown in the Figure 2.16.

It is important to have a general idea about the mineral component of the shale for kerogen isolation. For Green River shale, calcite and silicates constitute around 85% of the mineral matter. The rest is organic matter (~15%) that contains kerogen and bitumen.



Figure 2.14: Set up for kerogen isolation at the geochemistry lab at UH.



Figure 2.15: Picture of the isolated kerogen from GR-1 shale

1	FILL HCI	27	FILL HF:HCI	53	FILL H ₂ O	79	FILL H ₂ O
2	DRAIN	28	DRAIN	54	DRAIN	80	DRAIN
3	FILL HCI	29	FILL HF:HCI	55	FILL H ₂ O	81	FILL HCI
4	TIME/DRAIN	30	TIME/DRAIN	56	DRAIN	82	DRAIN
5	FILL HCI	31	FILL HCI	57	FILL NH₄OH	83	FILL H ₂ O
6	TIME/DRAIN	32	DRAIN	58	DRAIN	84	DRAIN
7	FILL H ₂ O	33	FILL H ₂ O	59	FILL H ₂ O	85	FILL H ₂ O
8	DRAIN	34	DRAIN	60	DRAIN	86	DRAIN
9	FILL H ₂ O	35	FILL H ₂ O	61	FILL H ₂ O	87	FILL CrCl ₂
10	DRAIN	36	DRAIN	62	DRAIN	88	DRAIN
11	FILL HCI	37	FILL NH ₄ OH	63	FILL HF:HCI	89	FILL HCI
12	DRAIN	38	DRAIN	64	TIME/DRAIN	90	DRAIN
13	FILL HCI	39	FILL H ₂ O	65	FILL HCI	91	FILL CrCl ₂
14	TIME/DRAIN	40	DRAIN	66	DRAIN	92	DRAIN
15	FILL HCI	41	FILL H ₂ O	67	FILL HF:HCI	93	FILL HCI
16	TIME/DRAIN	42	DRAIN	68	TIME/DRAIN	94	DRAIN
17	FILL H ₂ O	43	FILL HF:HCI	69	FILL HCI	95	FILL CrCl ₂
18	DRAIN	44	DRAIN	70	DRAIN	96	DRAIN
19	FILL H ₂ O	45	FILL HF:HCI	71	FILL HCI	97	FILL HCI
20	DRAIN	46	TIME/DRAIN	72	DRAIN	98	DRAIN
21	FILL NH₄OH	47	FILL HCI	73	FILL H ₂ O	99	FILL H ₂ O
22	DRAIN	48	DRAIN	74	DRAIN	100	DRAIN
23	FILL H ₂ O	49	FILL H ₂ O	75	FILL H ₂ O	101	FILL H ₂ O
24	DRAIN	50	DRAIN	76	DRAIN	102	DRAIN
25	FILL H ₂ O	51	FILL HCI	77	FILL HCI	103	FILL H ₂ O
26	DRAIN	52	DRAIN	78	DRAIN	104	DRAIN

Figure 2.16: Automated workflow for kerogen isolation

2.8 SEM imaging

The SEM (Scanning Electron Microscope) provides one of the useful techniques for micro-structural characterization for shales. One can produce a highly magnified image by using a focused beam of high energy electrons instead of light. The incident electrons lose energy and produce various signals. These signals include secondary electrons, backscattered electrons, and X-rays (Goldstein, 2003). Secondary electrons produce SEM images that show the morphology and topology of the sample surface, whereas backscattered electrons show the image contrast in position. X-rays are useful for elemental analysis. Many researchers have used the SEM technique to characterize the microstructure of shales (e.g., Sondergeld et al., 2010, Slatt and O'Brien, 2011; Curtis et al., 2011, and Milliken et al., 2013). In SEM, a fine probe of electrons with energies typically up to 40 keV is focused on a sample. Various signals are generated as a result of the impact of the incident electrons, which are collected to form an image or to analyze the sample surface. These are mainly secondary electrons, with energies of a few tens of eV, high-energy electrons backscattered from the primary beam and characteristic X-rays (Bogner et al., 2007). Backscattered scanning electron microscopy (BSE) reveals the minerals, textures, and fabrics of sediments and rocks in much greater detail (Krinsley et al., 2005).

Figure 2.17 shows the SEM machine located at the TX Super Conducting lab at UH. The essential components of a SEM include emission source or gun, electron lenses, sample chamber, and detectors. The sample is first carbon coated to make it conductive. Figures 2.18 and 2.19 show the back scattered SEM images of GR-1 before and after maturation. The kerogen is in solid form before maturation and void space is created after maturation. This additional pore space is known as the organic porosity. In the Figure 2.19b, the kerogen becomes softer due to maturation. Figure 2.20 show the back scattered SEM image for IR-1 matured shale. Pyrite crystals are clearly visible on the image. Figures 2.21 and 2.22 show the back scattered SEM images of matured and immature kerogen for GR-1 and IR-1 samples respectively.



Figure 2.17: Picture of SEM at Texas Super conducting lab at UH





Figure 2.19: SEM images of GR-1 shale (a) before maturation and (b) after maturation



Figure 2.20: Back scattered SEM image of IR-1 matured shale



Figure 2.21: SEM images of kerogen for (a) immature GR-1 and (b) mature IR-1



Figure 2.22: SEM images of kerogen for (a) immature GR-1 and (b) mature IR-1

2.9 Micro-CT scan

Micro-CT is a non-destructive technique that can provide information on finescale laminations and fracturing at a resolution of 10-40 microns. With CT scanning, linear attenuation coefficients (corresponding to small regions represented by voxels) are determined. These are normally expressed on a standardized scale as CT numbers (Watson and Mudra, 1994). CT images from a single scan do not provide measures of immediate use for determining basic porous media properties, although they can provide a quantitative indication of density. However, multiple scans with different saturating fluids can provide quantitative estimates of porosity and saturations. A stack of 2-D slices constitutes a 3D image. Within the slice, the data are arranged in a 2D array of pixels. A pixel with the third dimension, which is the distance between two consecutive slices, is called a voxel (Silin and Kneafsey, 2012).



Figure 2.23: Picture of the micro-CT scan machine at the Colorado School of Mines.


Figure 2.24: (a) micro-CT scan image of GR-1 shale (b) SEM images

An X-ray source is used for CT scanning (Figure 2.23). The sample is kept opposite to the source and rotated for few hours. The machine takes hundreds of 2D images of the sample. These images are constructed as 3D using software. Figure 2.24a shows the CT scan image of GR-1 immature shale and Figure 2.24b shows the SEM images of the same sample.

2.10 FTIR for mineralogy

There are mainly two ways of determining the mineralogy for rocks: (1) XRD (X-Ray Diffraction) and (2) FTIR (Fourier Transform Infrared spectroscopy).

FTIR is based on the absorption of the infrared energy as a function of the wave number or frequency. The infrared absorption bands identify specific molecular components and structures. When infrared energy passes through a sample, energy at certain frequencies is absorbed by the molecule. The optical absorption spectrum obtained is characteristic of the particular molecule and its validation mode. FTIR contains a fixed mirror, a movable mirror, and a beam splitter. The beam splitter splits the incoming infrared into two parts: one is directed towards the fixed mirror and the other on the moving mirror. If the two mirrors are at equal distance from the beam splitter, all the reflected infrared energy is in phase and they interfere either constructively or destructively. A series of constructive and destructive interference is generated depending on the position of the moving mirror and on the reflected infrared energy. A fast Fourier transform is used to convert the pulse to its spectral components. FTIR absorbance spectra for the Green River shale samples are shown in the Figure 2.25. The position of the amplitude peaks in the spectra determines the minerals that are present (Sondergeld and Rai, 1993).



Figure 2.25: Spectra from FTIR analysis for GR1 immature and mature shale samples

2.11 XRD analysis

X-ray diffraction is useful for determining the arrangement of atoms in the mineral. XRD is useful for identification and quantification of minerals in clay rich rocks (Srodon et al., 2001). Minerals do have a crystal lattice structure. When a focused X-ray beam interacts with these planes of atoms, part of the beam is transmitted, part is absorbed by the sample, part is refracted and scattered, and part is diffracted. X-rays are diffracted by each mineral differently, depending on what atoms make up the crystal lattice and how these atoms are arranged. Figure 2.26 shows the diffractograms for the Green River shale sample before and after pyrolysis.



Figure 2.26: XRD diffractograms for GR-1 before and after pyrolysis

Different minerals such as quartz, calcite, dolomite, K-feldspar, illite/smectite have been identified from the peaks in the diffractograms. The organics have been identified at 16^0 of 2 theta. All the intensities of the peaks remain same before and after pyrolysis except for organics and Feldspar (at around 26 of 2 theta). We know that some of the organics are lost after pyrolysis, but it's interesting to see decrease in Feldspar peak after pyrolysis.

2.12 Conclusions

Rock-eval pyrolysis is carried out on the shale samples to determine the current level of maturity. Anhydrous pyrolysis is carried out on an immature organic rich Green River shale sample. The sample is heated at 350C for three days. Hydrocarbon induced cracks are visible on the sample after pyrolysis. Large quantities of kerogen is transformed to oil/gas during maturation.

Micro-structural characterization of the shales show that the hydrocarbon induced micro cracks are connected in the three dimensional space.

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Rock physics analysis

3.1 Abstract

This chapter discusses the porosity and ultrasonic measurements carried out on the Green River shales and Irati shales and also on the kerogen isolated from these samples. The porosity of the immature Green River shale is around 1%, and after cooking it is found to be 7%. This porosity is known as the organic porosity as it is developed during maturation. Ultrasonic velocities are measured on the shale samples. Elastic constants and Thomsen's anisotropic parameters are estimated from the velocity measurements. The major change is decrease in P-wave anisotropy (60%) after maturation. It is evident that the micro cracks generated during maturation do not have any effect on the seismic anisotropy.

Porosity and ultrasonic measurements are also carried out on the kerogen isolated from immature Green River shale and matured Irati shale samples. Bulk modulus of kerogen is estimated by inverting Gassmann equation, Voigt and Reuss bounds. The bulk modulus changes from 4-5 GPa.

An attempt also made to understand the effect of kerogen content and its maturity on seismic velocities and anisotropy from the published data. It is observed that seismic anisotropy has different trends based on kerogen maturity. Though it seems to be that high anisotropy is caused by more presence of kerogen, but it is not the same case for every shale. Ultrasonic measurements are conducted while heating the sample upto 150° C and observed that the velocities decrease with the increase of temperature.

3.2 Introduction

Shales constitute about 75% of sedimentary basins (Vernik and Nur, 1992). But our understanding of seismic anisotropy caused by shales is still inadequate (Thomsen, 1986; Sayers and Kachanov, 1991). One of the reasons for this is shales are rarely cored from the wells. One of the important reasons for shale anisotropy is organic richness or kerogen content and the physiochemical interactions with fluids (Meissner, 1984). Regional understanding of the distribution of organic matter and its level of maturity is important for oil and gas generation and its migration in a basin (Vernik and Nur, 1992). The effect of organic matter and its maturity on seismic velocities and anisotropy is useful for (1) interpreting seismic reflection data to identify sweet spots (2) useful for interpretation of high frequency VSP data and also (3) sonic data. The degree of anisotropy depends on microstructure, pressure and frequency. However, care must be taken when interpreting velocity anisotropy at low frequencies when compared those at high frequencies from the lab measurements.

Seismic anisotropy in shales is caused by (1) preferential orientation of minerals (2) microcracks and also due to (3) lenticular distribution of organic matter. Low elastic wave velocity in source rocks have attributed to high organic matter content and over pressured state (e.g., Meissner, 1978; Mendelson and Toksoz, 1985).

3.3 Porosity measurements

The porosity of the rock samples can be measured using He porosimeter (Figure 1). The apparatus uses gas expansion method. When we use gas, it escapes the capillary effect and the reaction with the grains of the rocks. This does not happen for liquids. Thus gas pressure can actually represent the void space of rock, i.e., porosity.

The equation for this method is:

$$\Phi = (\mathbf{V}_{\mathrm{b}} - \mathbf{G}) / \mathbf{V}_{\mathrm{b}} \tag{1}$$

Where, Φ =porosity, V_b=bulk volume of the rock and G=grain volume. We can measure the bulk volume by measuring the cylinder sample's length and diameter. Then we need to find out grain volume (G).

Gas expansion method is based on Boyle's law (Draper, 1861). This law states that for a certain amount of ideal gas (helium), if the temperature is constant, the product of pressure and volume remains constant:

$$PV = constant$$
 (2)

A schematic for the He porosimeter is shown in the Figure 1. Helium gas can penetrate through the smallest void space in a rock. The Vander walls diameter of the He molecule is 140 pm (1 pm= 10^{-12} m) Here, R and C are the reference cell and chamber section (with sample) respectively. By calibration with billets of standard volume, we can measure volumes of R and C. The grain volume (G) of the rock can be estimated from the following expression:

$$G = R + C - R(P_0/P) \tag{3}$$

Where, $P_0=100$ psi, P=the amount of pressure after opening the bridge valve. P gives the porosity of the rock as other parameters are constant.

We need to maintain the system in isothermal condition during the experiment. It is observed that the length of the experiment may take longer time for shales because of micro porosity and very low permeability (Xuan and Han, 2012).



Figure 3.1: Schematic showing the working of He porosimeter



Figure 3.2: Picture of the He porosimeter at the Rock Physics Lab at UH

Table 3.1 shows porosity and grain densities for the kerogen samples. High porosities are observed for kerogen samples. This is because the kerogen samples are prepared from powder. The samples are molded in cylindrical shape from the powder.

Kerogen sample	Porosity (%)	Grain density (g/cc)
Green River immature (GR-1)	36	1.089
Irati cooked (IR-1)	41	1.337

Table 3.1: Porosities and grain densities of the kerogen samples

Table 3.2 shows the porosities and bulk densities of Green River and Irati shale samples. All these samples have low porosities (<5%). The GR-1 shale, which has around 16% TOC, has low bulk density of 1.79 g/cc.

Shale sample	Porosity (%)	Bulk density (g/cc)
Green River immature (GR-1)	1	1.79
Green River immature (GR-2)	4.5	2.26
Green River immature (GR-3)	0.5	2.25
Irati cooked (IR-1)	2.7	2.21

 Table 3.2: Porosities and grain densities of the shale samples

3.4 Ultrasonic measurements on shales

3.4.1 Core sampling and experimental procedure

We received a big junk of Green River formation core from the Colorado School of Mines. We cored the core plugs at the Rock Physics Lab (RPL). We cored 3 suites of plugs, each consists of one vertical (0^0) and horizontal plug (90^0) . Each suite has different amount of TOC. GR-1 has 16%, GR-2 has 11.5% and GR-3 has 6.5%. We also received one vertical cooked plug of Irati shale (IR-1) from Petrobras. IR-1 has 13.5% of TOC. All these plugs are cored with a diameter of around 1.5 inch and length of around 1.5-2.0 inches.

Ultrasonic measurements are carried out on horizontal plugs of Green River shale and vertical plug of Irati shales. We used the pulse transmission technique for ultrasonic measurements. It has around 1 MHz central frequency for P-waves and 0.7 MHz central frequency for S-waves. The accuracy of velocity measurements is about 1% for P-waves and about 2% for S-waves. A single plug method proposed by Wang (2002) has been used. Many researchers also used the same method for anisotropy of shales (e.g. Yan et al., 2013; Sondergeld and Rai, 2011). This method uses only one sample to measure the velocities required to derive the five independent elastic constants for TI materials. Piezoelectric transducers are fitted to the top, bottom, and sides of the cylindrical sample (Figure 3.3). This method uses a horizontal core plug that has more permeability than the vertical plug, hence best suitable for shales. This method reduces the sample preparation time and time taken for velocity measurements. Velocities are measured upto at a confining pressure of 5000 psi.

We can derive the five elastic constants using velocities and densities. For a horizontal plug, from a TI material, the five elastic constants are given by:

$$C_{33} = \rho V_{p0}^{2}$$
 (4)

$$C_{11} = \rho V_{p90}^{2}$$
 (5)

$$C_{44} = \rho V_{sv90}^{2}$$
 (6)

$$C_{66} = \rho V_{sh90}^{2}$$
(7)

$$C_{13} = \{ [(4\rho V_{p45}^2 - C_{11} - C_{33} - 2C_{44})^2 - (C_{11} - C_{33})^2]/4 \}^{1/2} - C_{44}$$
(8)

The anisotropy can be calculated using Thomsen's anisotropic parameters (Thomsen, 1986) and are given by:

$$\varepsilon = (C_{11} - C_{33})/2C_{33} \tag{9}$$

$$\gamma = (C_{66} - C_{44})/2C_{44} \tag{10}$$

$$\delta = \{ (C_{13} + C_{44})^2 - (C_{33} - C_{44})^2 \} / \{ 2C_{33}(C_{33} - C_{44}) \}$$
(11)

Vernik and Nur (1992) observed from Bakken shale lab measurements that the anisotropy is caused by organic matter as an amorphous substance distributed as microlaminae and lenticular lenses along the bedding plane and also can undergo some liquefaction with increase of temperature. Velocities and anisotropy of organic rich shales have been studied in the lab (e.g. Yan et al., 2012; Sondergeld and Rai, 2011; Vernik and Liu, 1997; Vernik and Nur, 1992). Figure 3.3 shows experimental setup for the ultrasonic measurements at the rock physics lab.



Figure 3.3: (a) Picture showing the shale sample in a transducer jacket (b) Ultrasonic setup with the sample jacket connected to all transducers



Figure 3.4: Variation of velocities with confining pressure for Green River-1 (immature) shale

The ultrasonic measurements on GR-1 show that the confining pressure has an effect on the velocities. The velocities increase with the increase of pressure. This can be caused by due to the closure any microcracks.





The plot between elastic constants and confining pressure is shown in Figure 3.5. The constant C11 which depends on Vp along horizontal layering is higher than the other elastic constants. All the constants are increasing with the pressure except C13, which is decreasing after 2000 psi.



Figure 3.6: Plot between anisotropic parameters and confining pressure for Green River-1 (immature) shale

Figure 3.6 shows the plot between Thomsen's anisotropic parameters and confining pressure. Shear wave anisotropy is greater than the P-wave anisotropy. The anisotropic parameters decrease with the confining pressure.





The ultrasonic measurements on GR-2 show that the confining pressure does not have much effect on the velocities. The velocities slightly increase with the increase of pressure. This sample has around 11.5% of TOC.





The plot between elastic constants and confining pressure is shown in Figure 3.8. The constant C11 which depends on Vp along horizontal layering is higher than the other elastic constants. All the constants are increasing with the pressure.



Figure 3.9: Plot between anisotropic parameters and confining pressure for Green River-2 (immature) shale

Figure 3.9 shows the plot between Thomsen's anisotropic parameters and confining pressure. P-wave has around 30% anisotropy. The anisotropic parameters decrease with the confining pressure.



Figure 3.10: Variation of velocities with confining pressure for Green River-3 (immature) shale

The ultrasonic measurements on GR-3 show that the confining pressure does not have much effect on the velocities. The velocities slightly increase with the increase of pressure. This sample has around 6.5% of TOC.



Figure 3.11: Plot between elastic constants and confining pressure for Green River-3 (immature) shale

The plot between elastic constants and confining pressure is shown in Figure 3.11. The constant C11 which depends on Vp along horizontal layering is higher than the other elastic constants. All the constants are increasing with the pressure.



Figure 3.12: Plot between anisotropic parameters and confining pressure for Green River-3 (immature) shale

Figure 3.12 shows the plot between Thomsen's anisotropic parameters and confining pressure. P-wave has around 18% anisotropy. The anisotropic parameters decrease with the confining pressure. Thomsen's parameter δ has a negative value.



Figure 3.13: Variation of velocities with confining pressure for Irati-2 (immature) shale

Irati-2 is a vertical sample, so we cannot measure anisotropy. The ultrasonic measurements on IR-2 show that the confining pressure does not have much effect on the velocities. The velocities slightly increase with the increase of pressure. This sample has around 8.5% of TOC.





The plot between elastic constants and confining pressure is shown in Figure 3.14. All the constants are increasing with the pressure.



Figure 3.15: Variation of velocity with TOC for the three Green River shale samples

3.4.2 Effect of TOC on velocities

The effect of TOC on seismic velocities for the Green River shale samples is shown in the Figure 3.15. P-wave velocities decrease with the increase of TOC amount. But, shear waves have a peculiar behavior as shown.

The wave propagation of elastic waves for GR-1 shale sample at 3000psi confining pressure is shown in Figure 3.16. The medium is considered as VTI. The black curves are isotropic and colored curves are anisotropic. We observed that the wave propagation is affected by the presence of lenticular/layered structure of TOC.



Figure 3.16: Seismic wave propagation for GR-1 shale sample. (a) P-wave (b) S-waves.

3.5 Ultrasonic measurements on kerogen

3.5.1 Sample preparation

The kerogen isolated from Green River-1 (immature) and Irati-1 (mature) shales have been used for ultrasonic measurements. Isolated kerogen is in powder form (Figure 3.17a). It is not possible to carry out velocity measurements on powder. So, we molded the powder into a cylindrical form using a vase, cylindrical container and steel bullets as shown in Figure 3.17b. Cylindrical kerogen samples are shown in the Figure 3.17c.



Figure 3.17: (a) kerogen powder (b) set up for kerogen sample preparation (image courtesy from Fuyong Yan) (c) molded kerogen samples

3.5.2 Equipment and measurement procedure

The bench top ultrasonic measurement system specially designed for kerogen is shown in the Figure 3.18. Both P and S waves are measured on the dry kerogen samples under the axial pressure from 2860 psi to 286 psi. The pressure is controlled by gas regulator system. After recording the ultrasonic measurements on the dry samples, the system is vacuumed and saturated with distilled water.



Figure 3.18: Bench top setup for kerogen ultrasonic measurements

After 1-4 hours of saturation, we observed the strong signal indicating the full saturation of the sample. Pore pressure is maintained at 286 psi. As the pressure reached to equilibrium, both P and S waves are recorded. After ultrasonic measurement on saturated kerogen sample, the kerogen sample is taken out carefully to keep the cylindrical form. The saturated sample is weighed. After weighing, the saturated sample is put into oven to dry for 48 hours at 40-50^oC. The dried sample is weighed again to see if the water is completely dried out. Figure 3.19 shows the recorded P waveforms for Irati kerogen measurements.



Figure 3.19: P waveforms for Irati kerogen measurements

The ultrasonic measurements are repeated again for kerogen samples after saturating with Silicone oil. After few hours of saturation, both P and S wave velocities are recorded. The pore pressure is kept at 286 psi. The velocity of Silicone oil is measured using the bench top set up as shown in the Figure 3.20a. The velocity and density of Silicone oil is estimated to be 1.005 km/s and 0.946 g/cc respectively.



(b)

(~)	
Oil velocity	1.005 km/s
Oil density	0.946 g/cc
Temperature	21.1 C
Pressure	Atmospheric

Figure 3.20: (a) Setup for Silicone oil velocity measurement (b) Properties of Silicone oil



Figure 3.21: Cross plot between velocities and differential pressure for GR-1 kerogen



Figure 3.22: Cross plot between bulk modulus and differential pressure for GR-1 kerogen

3.5.3 Kerogen measurement results

Figures 3.21 and 3.23 show the velocities for GR-1 and IR-2 kerogen samples. The water saturated kerogen has around 1.9 km/s velocity, oil saturated kerogen has around 1.5 km/s, and the dry kerogen has a velocity around 1.2 km/s. P-wave velocities increase slightly after 1500 psi differential pressure. It became difficult to pick up the first arrivals of S waves especially at low pressures. The velocity of dry kerogen is estimated around 0.7 km/s. The S wave velocities for Silicone oil and distilled water saturated kerogen remains the same as the densities of both the saturates is close to 1 g/cc. S wave velocities for saturated kerogen change from 0.5-0.6 km/s.



Figure 3.23: Cross plot between velocities and differential pressure for IR-2 kerogen



Figure 3.24: Cross plot between bulk modulus and differential pressure for IR-2 kerogen

The bulk modulus of kerogen is estimated by inverting the Gassmann equation, Voigt and Reuss bounds. The Voigt and Reuss bounds are given by (Mavko et al., 2008):

$$\frac{1}{K_{sat}} = \frac{1-\emptyset}{K_m} + \emptyset/Kf \tag{12}$$

$$Ksat = (1 - \emptyset)Km + \emptyset Kf \tag{13}$$

Where, Km is mineral bulk moduli (kerogen is the mineral in this case), Kf is fluid bulk moduli, Φ is porosity and Ksat is the bulk moduli of the saturated kerogen sample. If there is no measurement error, the inverted Km by Reuss bound is the highest possible value for Km and the inverted Km by Voigt bound is the lowest possible value for Km as shown in the Figures 3.22 and 3.24. The relative small difference between Km inverted by Reuss bound and that inverted by Voigt bound shows that uncertainty due to rock physical model is not significant (Yan and Han, 2013). The smaller is the kerogen modulus, the smaller is the difference. It is reasonable and expected that the inverted Km values don't have trends varying with differential pressure. The bulk modulus of kerogen is found to be between 2-9 GPa. For matured IR-2 kerogen, there is less difference for bulk modulus when the sample is saturated with Silicone oil.

3.6 Before and after maturation

The main research goal of my dissertation is to understand how the kerogen maturity will affect the seismic, petrophysical and micro-structural properties. To achieve this goal, organic rich immature Green River-1 (GR-1) shale plug has been selected. The schematic of the workflow is shown in the Figure 3.25. I measured the bulk density, porosity of the GR-1 shale. I also measured the ultrasonic velocities and estimated the anisotropy. SEM imaging and micro-CT scanning is also carried out on the immature GR-1 shale plug for micro-structural characterization. Then, the sample is subjected to anhydrous pyrolysis for artificial maturation. The sample is heated at 350^oC for three days. Hydrocarbon induced cracks are observed on the matured sample (Figure 3.26b). The sample is compacted as shown in the Figure 3.26c and it now resembles the post maturation stage. As the matured sample has an ellipsoidal shape, it is reshaped into a cylindrical shape. Ultrasonic and porosity measurements are carried out on the post matured compacted reshaped sample.


Figure 3.25: Schematic showing the workflow for GR-1 shale plug



Figure 3.26: Pictures showing the GR-1 shale (a) before maturation (b) after maturation and (c) after post maturation

Table 3.3 shows the changes in the rock properties before and after post maturation for the GR-1 shale sample. Around 7.8% increase on bulk density is observed. And, grain density is increased by around 15%. This change may be due to some of the lighter kerogen transformed to heavier pyrite or bitumen during maturation. The porosity is increased by 600% and this porosity might have been developed in the organic matter hence also known as organic porosity.

Rock Property	Before	After Maturation	Post Maturation	
	Maturation		(Reshaped)	
Weight (gm)	79.74	70.35	30.08	
TOC (wt%)	27.5		18	
Bulk density (g/cc)	1.79		1.93	
Grain density (g/cc)	1.80		2.07	
Porosity (%)	1		7	

Table 3.3: Rock properties before and after post maturation for GR-1 shale

TOC is also measured before and after maturation. Initially, GR-1 has 27.5% of TOC and after cooking, it dropped to 18% in weight. This remaining TOC might be bitumen. Rock-eval pyrolysis is also carried out before and after maturation. Figure 3.27a shows modified van Krevelen diagram for GR-1 shale. It shows the relationship between hydrogen index (HI) and oxygen index (OI). There is a drastic drop in the hydrogen content of the shale after maturation. Figure 3.27b shows the relationship between HI and Tmax observed from rock-eval pyrolysis. This plot clearly indicates that GR-1 shale has fallen in the matured window after cooking.



Figure 3.27: Changes in geochemical properties before and after maturation (a) van Krevelen diagram (b) HI vs. Tmax



Figure 3.28: SEM images for GR-1 shale (a) before and (b) after maturation

SEM images are compared for GR-1 before and after maturation and shown in the Figure 3.28. Organic matter is in the solid form (Figure 3.28a) before cooking the sample. Additional pore space or micro-cracks are observed on the cooked sample (Figure 3.28b). This pore space is known as organic porosity as it is developed within the organic matter.



Figure 3.29: Micro-CT scan images for GR-1 shale after maturation (a) 3D view (b) 2D view

Figure 3.29 shows the micro-CT scan images of the GR-1 shale after maturation. Hydrocarbon induced cracks are clearly visible on the images. It is interesting to note that these micro cracks are connected in 3D space. The red square box shown in the Figure 3.29b is the location of the SEM image shown in the Figure 3.28b.



Figure 3.30: Micro-CT scan images for GR-1 shale after post maturation (a) 3D view (b) 2D view

The matured GR-1 shale sample is compacted and reshaped to a cylindrical shape with 1 inch diameter. Figure 3.30 shows the micro-CT scan images of post matured reshaped GR-1 sample. The vertical crack visible on the images is a man made crack. The white color dots are pyrite. Interestingly, all the hydrocarbon induced cracks are closed after compaction.

Figures 3.31 and 3.32 show the recorded P waveforms before and after maturation in both 0^0 and 90^0 directions.



Figure 3.31: P_0 waveforms before and after maturation recorded at (a) 1000psi (b) 3000psi (c) 5000psi



Figure 3.32: P_{90} waveforms before and after maturation recorded at (a) 1000psi (b) 3000psi (c) 5000psi



Figure 3.33: Variation of velocities with confining pressure before and after maturation for GR-1 shale

Ultrasonic measurements are carried out on the post matured GR-1 sample. Figure 3.33 shows the velocities for the immature and post mature GR-1 shale. Velocities increase with the increasing confining pressure. Vp90 and Vp45 decrease after maturation. The post matured Vp0 increases after 3000 psi.

Both types of shear wave velocities increase after post maturation. This increase might be due to increase in bulk density after maturation (7.8% increases).



Figure 3.34: Variation of Thomsen's anisotropic parameters with confining pressure before and after maturation for GR-1 shale

The Thomsen's anisotropic parameters calculated before and after post maturation for GR-1 are shown in the Figure 3.34. Anisotropy decreases after maturation. It indicates that there is no effect of hydrocarbon induced cracks on seismic velocities. P-wave anisotropy parameter, Epsilon decreases by 60% after post maturation. A significant change in anisotropy is observed after maturation.

3.7 Effect of kerogen and its maturity on seismic anisotropy

In this section, an attempt has been made to understand how the seismic anisotropy is affected by kerogen and its level of maturity for organic-rich shales. The data used in this analysis is extracted from the published literature. The data is collected from the publications of Vernik and Liu (1997), Vernik and Landis (1996) and from Vernik and Nur (1992). The data set include Bakken shale, Bazhenov shale, Monterey shale, Niobrara formation, Kimmeridge shale, Woodford and Lockatong shales.



Figure 3.35: Relationship between Thomsen's anisotropy and hydrogen index for different shales



Figure 3.36: Relationship between Thomsen's anisotropy and volume of kerogen for different shales

Thomsen's anisotropic parameters, kerogen content and hydrogen index (HI) has been reported for the above mentioned shales in the published literature. HI is an important indicator of level of maturity for organic rich shales (Price et al., 1984). Figure 3.35 shows the relation between Thomsen's anisotropic parameters and HI for the shales. HI values between 0 to 200 are treated as post mature or shale gas window. HI values between 200 and 500 are treated as mature or shale oil window. HI values from 500 and above are treated as immature or oil shale window. Figure 3.36 shows all the data points for three Thomsen's anisotropic parameters for all the shales.



Figure 3.37: Relationship between Thomsen's anisotropy and hydrogen index for Green River shale and other shales

The epsilon value before and after maturation for GR-1 is also shown in the Figure 3.37. Epsilon (P wave anisotropy) decreases after maturation. It is also observed that the anisotropy behaves differently for three stages of kerogen maturity. For shale gas window, the anisotropy decreases with the increase of maturity.

Figure 3.38 shows the same relationship between anisotropy and HI, color coded with kerogen volume. It is observed for oil shales (immature) that even high amount of kerogen (>15%) has low anisotropy (<20%), e.g. Monterey shale. One of the causes is that this shale has high amounts of silica. So, mineralogy also play an important role for anisotropy.



Figure 3.38: Relationship between Thomsen's anisotropy and hydrogen index for different shales color coded with kerogen volume

I tried to look at the dominant mineralogy of the shales. I found that organic-rich clay shales have higher Epsilon (>20%) (e.g., Bakken shale and Kimmeridge shales). Other shales like Bazhenov shale (siliceous), Monterey shale (silica/cherty) and Lockatong shales (fine grained siltstone) do have low epsilon (<20%) even if they are organic rich. It is a key observation that the morphology and structure of organic matter (kerogen) changes with the associated sediment deposition. Kerogen has lenticular/layered structure (anisotropic) when deposited with clay. it has spherical/amorphous structure (isotropic) when deposited with silica and carbonates.



Figure 3.39: The relation between Vp/Vs and hydrogen index

The relationship between Vp/Vs and hydrogen index is shown in the Figure 3.39. The ratio remains flat in the matured and immature windows. Figures 3.40 to 3.42 show the relationships between elastic constants and hydrogen index for five different shales.



Figure 3.40: Relationship between C₃₃ and hydrogen index



Figure 3.41: Relationship between hydrogen index and (a) $C_{44}\left(b\right)\,C_{66}$





The analysis is carried out seperately for each window. Figure 3.43 shows the analysis in the shale gas window (HI=0-200). The anisotropy increases with the increase of HI. Figure 3.44 shows the analysis in the shale oil window (HI=200-500). No significant trend is observed between anisotropy and HI or bulk density in this window. This window is complex as the maturation currently taking place.



Figure 3.43: Relationship between Thomsen's parameters and (a) HI (b) Bulk density, for shale gas window (HI=0-200).



Figure 3.44: Relationship between Thomsen's parameters and (a) HI (b) Bulk density, for shale oil window (HI=200-500).



Figure 3.45: Relationship between Thomsen's parameters and (a) HI (b) Bulk density, for oil shale window (HI=500-800).

Figure 3.45 shows the immature window (HI=500-800). P-wave anisotropy (ϵ) increases with the increase of HI. Figure 3.46 shows the relationship between anisotropy and bulk density, kerogen volume for Eagle Ford shale data set from RPL. The bulk densities decrease with the increase of kerogen. The P-wave anisotropy parameter, ϵ increases with the increase of kerogen volume (low bulk density).



Figure 3.46: Relationship between Thomsen's parameters and (a) Bulk density (b) Kerogen volume, for RPL's Eagle Ford shale data (Data courtesy from Fuyong Yan).

An attempt has been made to understand the relationship between bulk densities, kerogen volume with the level of maturity for different shales (Figure 3.47). For matured shales (HI~0-450), the bulk density decreases with the increase of kerogen volume. All the matured shales have a bulk density more than 2.2 g/cc. It is observed that no significant relationship between bulk density and kerogen volume for immature shales (HI>450). All the immature shales have a bulk density lower than 2.2 g/cc.



Figure 3.47: Relationship between bulk density and kerogen volume color coded by HI for different shales.

Geological Elen	Seismic properties		
	Quartz	Low anisotropy	
Dominant mineralogy	Clay	High anisotropy	
	Calcite	Low anisotropy	
Fractures/Cracks	Stress/Tectonic related (vertical)	High anisotropy	
	HC generation related (horizontal)	High anisotropy	
Pressure	Normal pressure	High velocities	
	Over pressure	Low velocities	
	Immature	High anisotropy	
Kerogen and maturation	Mature	Low velocities	
	Over Mature	High velocities	

Figure 3.48: Chart showing the effect of geological elements or processes on seismic properties.

Figure 3.48 shows relationship between geological elements/processes and seismic properties. The seismic properties are affected by dominant mineralogical content in shale. Shales which have dominant mineralogy of quartz or calcite may have lower anisotropy because of their structure and the kerogen associated with these minerals also would have the similar isotropic structure, thus reducing the anisotropy. Clay rich shales do possess higher anisotropy due to the layered structure of clay platelets and the kerogen associated with clay deposition may also have lenticular or layered structure thus contributing to the increase in anisotropy. Cracks generated during hydrocarbon generation (maturation) also increase the anisotropy. These hydrocarbon induced cracks are almost parallel to the horizontal layering. Stress or tectonic related vertical fractures also increase seismic anisotropy.

Immature shales are under normal pressure regime and the pressure increases with the increase of kerogen maturity. Over pressure is caused by conversion of kerogen to oil and gas. When the transformation happens in a relatively fixed pore space, it exerts over pressure. This change in pressure regime caused by kerogen maturity also affects the seismic properties. Normal pressured regime generally has higher velocities than the over pressured regime. Amount of kerogen and its level of maturity also affect the seismic properties. Immatured and over matured shales may have higher anisotropy than the currently maturing shales.

Finally, a combination of different geological elements and processes contribute for the effect on seismic properties. These processes also vary from shale to shale, basin to basin or within the same basin.

3.8 Rock physics model

Voigt and Reuss bounds are the upper and lower bounds of a mineral composite. Bulk and shear moduli are calculated for GR-1 shale before and after maturation. These moduli are plotted against kerogen volume (Figure 3.49). Voigt and Reuss bounds are calculated for the shale. Kerogen and the rest of minerals (a combination of quartz and calcite) are considered for calculating the Voigt and Reuss bounds. The moduli fall very close to the Reuss bound.



Figure 3.49: Voigt and Reuss bounds for GR-1 shale sample. Relationship between kerogen volume and (a) bulk modulus, (b) shear modulus

Bulk and shear moduli also calculated for different shales and plotted against kerogen volume and shown in the Figure 3.50. The naturally matured shales have high moduli and low kerogen volume. Artificially matured GR-1 shale has low moduli. A significant change in moduli is observed between naturally matured and artificially matured shale samples. Bulk and shear moduli calculated in the vertical direction fall close to Reuss bounds.



Figure 3.50: Voigt and Reuss bounds for different sub-surface shale samples. Relationship between kerogen volume and (a) bulk modulus, (b) shear modulus

3.9 Low temperature ultrasonic measurements

Heating and ultrasonic measurements are carried out simultaneously on Green River shale (GR-1vertical). This is a vertical plug with 27.5% TOC and bulk density of 1.79 g/cc. The sample is heated from room temperature to 150° C in the apparatus. The recorded P waveforms are shown in the Figure 3.51.



Figure 3.51: P waveforms recorded at different temperatures

P and S wave velocities are recorded at different temperatures (Figure 3.52). Both P and S wave velocities decrease with the increase of temperature.



Figure 3.52: Variation of velocities with temperature for GR-1vertical sample

Vernik and Nur (1992) conducted similar temperature measurements on a matured Bakken shale (TOC=12.9%; HI=319; Bulk density=2.22 g/cc). Figure 3.53 shows the relationship between Vp/Vs with temperature for GR-1vertical and Bakken shale sample.



Figure 3.53: Relationship between Vp/Vs and temperature for GR-1vertical and Bakken shales

3.10 Discussion

Several properties are affected by the kerogen maturity. These properties include petrophysical, microstructural, ultrasonic and geochemical properties. The hydrocarbon induced cracks are visible on the artificially matured sample. All these cracks are parallel to bedding. In this experiment, these cracks are opened as no confining pressure is applied. This may be different for subsurface conditions. From CT-scan analysis, it is evident that these horizontal cracks are connected in 3D space, thus providing a pathway for hydrocarbon migration. In our study, we closed the cracks by applying confining pressure. The closed cracks have no significant effect on the seismic properties. A significant amount of porosity is developed during maturation (7%). This porosity is due to conversion of solid kerogen to liquid or gaseous hydrocarbons during maturation. Grain density also increased due to the decomposition of lighter kerogen during pyrolysis.

We also studied the effects of kerogen maturity on seismic properties from different shales around the world. These shales include Bakken shale, Eagle Ford shale, Woodford shale, Lockatong and Monterey shales from USA, Kimmeridge shale from North sea, and Bazhenov shale from Siberia. The study show that the seismic anisotropy is affected by each level of maturity and it also depends on other parameters such as dominant mineralogical composition, structure of kerogen, pressure regime, etc. For example, though Monterey shale has around 30% kerogen, but shows low anisotropy. This may be due to isotropic structure of kerogen associated with deposition of quartz.

3.11 Conclusions

Porosity measurements on the immature and matured shale show that a significant amount of organic porosity is developed after maturation. P-wave anisotropy (ϵ) decreased to 60% after maturation. This indicates that no effect of hydrocarbon induced cracks after compaction.

Porosity and ultrasonic measurements are also carried out on the kerogen isolated from immature Green River shale and matured Irati shale samples. The bulk modulus of kerogen is found between 3-5 GPa.

An attempt also made to understand the effect of kerogen content and its maturity on seismic velocities and anisotropy from the published data. Vp/Vs ratio and anisotropy are affected by the level of maturity. Temperature and ultrasonic measurements on Green

River shale show that the velocities decrease with the increase of temperature.

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Chapter 4

Understanding the effects of kerogen maturity for Bakken shale

4.1 Abstract

The conversion of kerogen to oil/gas will build up overpressure. Overpressure is caused by conversion of solid kerogen to fluid hydrocarbons in a relatively fixed pore space. The excess pressure caused by kerogen maturity does have impact on the seismic elastic properties. The wave propagation, velocities, anisotropy and AVO effects by kerogen maturation have been obtained as a function of initial kerogen content (immature), excess pore pressure (mature) for Bakken shale from Williston basin, USA. Our analysis shows that more matured shales are brittle and suitable for hydraulic fracturing for maximum production.

4.2 Introduction

Source rock maturity yields oil/gas which develops overpressure (e.g., Meisner, 1978; Luo and Vasseur, 1996). It is important to understand how the maturity of kerogen will affect the seismic properties that are of interest to geophysicists. Immature source

rocks are in the normal pressured regime and the pressure increases with maturity and over-matured source rocks will be in over-pressured regime (Figure 4.1).



Figure 4.1: Comparison between an immature and mature source rock.

Source rock maturity also yields additional cracks. Smectite to illite transition due to maturity also generate some free water in the formation. It is important to understand how the over-pressure caused by source rock maturation will affect the seismic properties.

The major seismic properties that are affected by source rock maturity:

- (1) *Velocity anisotropy*: Seismic velocity is dependent on the direction of the wave propagation.
- (2) *Q* (*or Attenuation*): Seismic energy will be attenuated due to fluids or cracks within the rock. Attenuation is inversely proportional to the quality factor (Q).

- (3) *Dispersion*: Seismic velocity is dependent on the frequency.
- (4) *Vp/Vs ratio (or Poisson's ratio)*: Vp/Vs is used as an indicator of presence of fluids in a rock. Poisson's ratio is an indicator of stiffness of the rock.

Experimental results show that kerogen in organic rich shales causes velocity anisotropy (e.g., Prasad et al., 2009; Vernik and Nur, 1992, Vernik, 1994).

4.3 Simple model for kerogen maturity (Carcione, 2000)

An immature source rock is considered as a viscoelastic transversely isotropic medium containing illite (clay) and kerogen (Figure 4.2). Illite is treated as transversely isotropic (TI) and kerogen as an isotropic medium. As the seismic wavelength is much larger than the thickness of the individual (illite/kerogen) layers, the medium behaves as a homogeneous, TI material whose stiffnesses can be calculated from Backus averaging (Schoenberg and Muir, 1989). When the kerogen to oil/gas conversion exceeds the rate of volume loss due to fluid flow, excess pore pressure is generated. The excess pore pressure can be estimated as a function of converting factor (Berg and Gangi, 1999). As the kerogen maturity increases, Kuster and Toksoz (1974) model is used to calculate the bulk modulus and density of the oil and kerogen mixture.



Figure 4.2: Schematic representation of kerogen maturity

4.4 Example: Bakken shale

We used the published ultrasonic and kerogen content information from Vernik and Nur (1994) for Bakken shale from Williston basin, USA. It is estimated that around 10 to 400 billion barrels of oil have been generated from Bakken shales and charged both conventional and unconventional plays in the basin (Jin et al., 2012). The source type of Bakken shale is mainly type I/II.

Velocities and densities of the media have been extracted from the published literature. The properties are summarized in Table 4.1.

Medium	V ₁₁	V ₃₃	V ₅₅	V ₆₆	V ₁₃	Density	Source
	(km/s)	(km/s)	(km/s)	(km/s)	(km/s)	(g/cc)	of info.
Illite	4.7	4.36	2.46	2.77	2.43	2.7	Vernik
							(1994)
Kerogen	2.6	2.6	1.2	1.2	1.97	1.4	Vernik
							(1994)
Oil	0.73	0.73	0	0	0.73	0.9	McCain
							(1984)

Table 4.1: Properties of the media used in the modeling

Figure 4.3 shows the published TOC (wt%) and bulk density values (filled blue circles) for Bakken shale. We calculated TOC from bulk densities of rocks, and densities of kerogen and illite. The best fit (open circles) line is obtained when TOC accounts for approximately 22% of kerogen.



Figure 4.3: Relation between density and TOC for samples of Bakken shale.

4.5 Elastic properties of immature Bakken shale

Experimental and calculated phase velocities (both Vp and Vs) are plotted with kerogen in the Figure 4.4. Both Vp and Vs decrease with increase of kerogen content. The difference between the model and experiment may be due to mineral composition. The actual Bakken shales may have other minerals such as quartz and calcite. But our model considers only illite (70%) and initial immature kerogen (30%) of each rock sample.



Figure 4.4: Bedding parallel (90^{0}) and bedding perpendicular (0^{0}) velocities for (a) compressional and (b) shear waves.

Figure 4.5 shows the Thomsen anisotropic parameters calculated from the experiments.


Figure 4.5: Thomsen's anisotropic parameters derived from the experiments

4.6 From immature to maturity of Bakken shale

As the source rock matures, the solid kerogen starts to transform to liquid oil. When this transformation happens in a relatively fixed pore space, excess pore pressure is generated. This excess pore pressure also generates micro-cracks which will act as conduits for the fluids to migrate.

The depth of Bakken shale varies from 3000 to 3400m in the study area. The lithostatic pressure (= ρzg) at a depth of 3.2km (z) for an average density of 2.4 g/cc (ρ) is equal to 75 MPa, where g is acceleration due to gravity. The hydrostatic pressure is equal to 31 MPa. So, the maximum possible pore pressure change (Δp) will be from hydrostatic to lithostatic, i.e., nearly 44 MPa. At this excess pressure, the rock may reach the fracture stage.

The initial content of kerogen is considered as 30%. A fraction of it changes due to maturation and kerogen to oil conversion generates excess pore pressure. This excess

pressure is calculated based on Berg and Gangi's (1999) relation (A-6). The amount of excess pressure generated due kerogen conversion is shown in the Figure 4.6a. About 35% of initial kerogen of 30% has to be converted to oil to generate fracture pressure of 44 MPa.

Kerogen conversion also increases the porosity. If we consider the initial porosity as the initial kerogen proportion K, the porosity increases from this value to K exp (Cp Δ p). Figure 4.6b shows the fraction of kerogen converted to porosity with excess pore pressure. The porosity increase at the fracture pressure (i.e. 44 MPa) is around 14% of the initial porosity.



Figure 4.6: Fraction of kerogen converted to (a) oil and to (b) porosity with excess pore pressure

The bulk, shear moduli and density of kerogen and oil composite is calculated using Kuster and Toksoz (1974) spherical inclusion model. These values are used to derive the complex stiffness elastic moduli (A-3) of the composite rock. Wave phase velocities have been derived using A-4. Wave velocities with excess pore pressure are shown in the Figure 4.7. Both Vp and Vs decrease with the increase of excess pore pressure.

Figure 4.8 shows the anisotropic parameters with excess pore pressure. The anisotropy increases with the pore pressure due to kerogen to oil conversion.



Figure 4.7: Bedding normal (0^0) and bedding parallel (90^0) velocities for (a) P-wave and (b) S-wave, versus excess pore pressure, for an initial kerogen content of 30%.



Figure 4.8: Thomsen's anisotropic parameters with excess pore pressure.

4.7 Effect of kerogen maturity on wave propagation and AVO

We plotted the wave propagation for P, Sv and Sh waves by treating as VTI medium. For immature Bakken shale, we considered the velocities and anisotropy parameters for initial kerogen 30% (Figure 4.9 a&b). We considered the velocities and anisotropic parameters when the excess pore pressure reached 44 MPa (Figure 4.9 c&d). It is observed that the maturity affects the wave propagation.



Figure 4.9: Anisotropic wave propagation for Bakken shale for (a) immature P (b) immature Sv and Sh (c) mature P and (d) mature Sv and Sh waves.

We also computed the effects of maturity on AVO (Amplitude Variation with Offset). AVO is caused by the fact that the reflected energy depends not only on the acoustic impedance but also on the angle of incidence of the reflecting energy. Change of amplitude in the rock is linked to fluid content of the rock. Mississippian Bakken shale is overlain by Lodgepole limestone formation in the Williston basin. The Lodgepole formation is considered to be isotropic and its properties are, Vp=5.28 km/s, Vs=2.81 km/s and density=2.5 g/cc (Bandyopadhyay, 2009). Shuey's (1985) two term

approximation is used to calculate the P wave reflectivities for both immature and mature Bakken shale (Figure 4.10). For immature, it's a typical class IV AVO. The reflective amplitude increases from immature to mature as shown in the Figure 4.10.



Figure 4.10: Variation of PP reflectivity for mature and immature Bakken shale.

4.8 Effects of kerogen maturity on geomechanical properties

Hydraulic fracturing is necessary for production from the shale. Hydraulic fracturing is successful for more brittle shale rocks (Rickman et al., 2008). The concept of brittleness combines seismic derived properties such as Young's modulus (E) and Poisson's ratio (υ). These two explain the rocks ability to fail under stress (E) and maintain a fracture (υ), once the rock fractures (Rickman et al., 2008). Higher acoustic impedance (Ip) also indicates brittleness. It is important to understand how the TOC and kerogen maturity will affect the geomechanical properties of shales. Higher Young's modulus and lower Poisson's ratio indicate that the rock is more brittle and prone for fractures after hydraulic fracturing. Brittleness index can be simplified as the ratio of these two parameters (=E/ υ) (Guo et al., 2012).

Figure 4.11 shows the cross plots between Young's modulus and Poisson's ratio (Figure 4.11a) and between acoustic impedance and Poisson's ratio (Figure 4.11b). The low TOC shales are more brittle. The cross plot between brittleness index and hydrogen index also confirm that more matured and low TOC shales are more brittle and suitable for successful hydraulic fracturing.



Figure 4.11: Cross-plots between (a) Young's modulus and Poisson's ratio (b) P-impedance and Young's modulus, color coded with TOC.



Figure 4.12: Cross-plot between brittleness index and hydrogen index, color coded with TOC.

4.9 Conclusions

The seismic properties of matured shale are expressed in terms of excess pore pressure. P and S wave velocities decrease and anisotropy increases with the increase of kerogen maturity. The wave propagation of elastic waves (especially P and Sv waves) is affected by kerogen maturity. AVO is also changed by maturity. Immature Bakken shale has class IV AVO and its amplitude is affected by kerogen maturity. More matured shales have high brittleness thus suitable for hydraulic fracturing for optimized production.

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4.11 Appendix

Illite is considered as transversely isotropic and kerogen is considered as isotropic and both of them act as viscoelastic TI medium. The stiffness for illite is given by (Carcione, 1998),

$$c_{I(I)} = \hat{c}_{I(I)} - D + BM_1 + \frac{4}{3}GM_2, \qquad I = 1, 2, 3,$$

$$c_{IJ} = \hat{c}_{IJ} - D + BM_1 + 2G\left(1 - \frac{1}{3}M_2\right),$$

$$I, J = 1, 2, 3; \qquad I \neq J,$$

$$c_{55} = \hat{c}_{55}M_2, \qquad c_{66} = \hat{c}_{66} + G(M_2 - 1),$$

......(A-1)

Where,

$$B = D - \frac{4}{3}G$$
$$D = \frac{1}{3}(2\hat{c}_{11} + \hat{c}_{33}), \qquad G = \frac{1}{3}(2\hat{c}_{55} + \hat{c}_{66}),$$

As the kerogen is considered as isotropic, each layer of kerogen is described by Lame parameters given by Carcione et al. (1998),

$$c_{13} = \rho_k \left(V_{11}^2 - \frac{4}{3} V_{55}^2 \right) M_1 - \frac{2}{3} \rho_k V_{55}^2 M_2,$$

$$c_{55} = \rho_k V_{55}^2 M_2,$$
 (A-2)

Where, V_{11} and V_{55} are high frequency P and S velocities, ρ_k is the density of kerogen. As the medium is isotropic, we know that $C_{11}=C_{33}=C_{13}+2C_{55}$ and $C_{66}=C_{55}$.

Backus averaging is used to get complex effective stiffnesses of a TI medium which is given by Schoenberg and Muir (1989),

$$C_{11}^{*} = \langle C_{11} - C_{13}^{2} C_{33}^{-1} \rangle + \langle C_{33}^{-1} \rangle^{-1} \langle C_{33}^{-1} C_{13}^{-1} \rangle^{2}$$

$$C_{33}^{*} = \langle C_{33}^{-1} \rangle^{-1} \langle C_{33}^{-1} C_{13}^{-1} \rangle^{-1}$$

$$C_{13}^{*} = \langle C_{33}^{-1} \rangle^{-1} \langle C_{33}^{-1} C_{13}^{-1} \rangle$$

$$C_{55}^{*} = \langle C_{55}^{-1} \rangle^{-1}$$

$$C_{66}^{*} = \langle C_{66}^{-1} \rangle^{-1}$$
(A-3)

Where,

 C_{ii}^{*} = complex elastic moduli of viscoelastic TI medium

 C_{ij} = elastic moduli of individual illite or kerogen

The eigen values of Christoffel matrix gives three different modes of propagation: quasi P wave (qP), quasi S wave (qS) and pure S wave. The velocities are given by,

$$V_{qS}(0) = V_{qS}(90) = \sqrt{c_{55}^*/\rho},$$

$$V_{qP}(0) = \sqrt{c_{33}^*/\rho}, \qquad V_{qP}(90) = \sqrt{c_{11}^*/\rho},$$

$$V_{S}(0) = \sqrt{c_{55}^*/\rho}, \qquad V_{S}(90) = \sqrt{c_{66}^*/\rho},$$
......(A-4)

From the complex moduli, we can deduce Thomsen's anisotropic parameters as given by Thomsen (1986),

$$\epsilon_{R} = \frac{c_{11\,R}^{*} - c_{33\,R}^{*}}{2c_{33\,R}^{*}}, \qquad \gamma_{R} = \frac{c_{66\,R}^{*} - c_{55\,R}^{*}}{2c_{55\,R}^{*}},$$

$$\delta_{R} = \frac{\left(c_{13\,R}^{*} + c_{55\,R}^{*}\right)^{2} - \left(c_{33\,R}^{*} - c_{55\,R}^{*}\right)^{2}}{2c_{33\,R}^{*}\left(c_{33\,R}^{*} - c_{55\,R}^{*}\right)}, \qquad (A-5)$$

Here the subindex R indicates the real part.

Berg and Gangi (1999) calculated the amount of excess pore pressure being generated by source rock due to maturity of kerogen, when it transforms to oil/gas. The effect of pressure on the kerogen conversion is negligible; the conversion of kerogen to oil generates excess pore pressure. The excess pressure generated depends on the amount of kerogen transformation (F), densities of kerogen and oil, and compressibilities of pore, oil and kerogen. The expression for excess pore pressure generated due to kerogen to oil conversion is given by,

$$\Delta p = \{(D-1)F\} / \{Cp + Ck - F[Cp + Ck - D(Cp + Co)]\} ------(A-6)$$

Where,

 $\Delta p = Excess in pore pressure, D = Ratio of densities of kerogen and oil,$ F = Kerogen to oil conversion factor, Cp = Pore space compressibility,Ck = Kerogen compressibility, Co = Oil compressibility

Chapter 5

Seismic and petrophysical characterization of Barnett shale

5.1 Abstract

It is important to understand the relationship between rock properties and seismic properties for successful characterization of shale gas reservoirs. The study area is from Barnett shale gas reservoir in the Fort Worth basin. The vitrinite reflectance (%Ro) is around 1.1-1.3, indicating the transition or wet gas window. The dataset include well logs from 3 wells and 3D seismic data. TOC log is generated using Delta log R technique, which used sonic and resistivity logs. TOC log is calibrated with the core measurements. The crossplots between TOC and AI (Acoustic Impedance) from the well logs indicate that both of them have an inverse relationship. Crossplots between AI and Young's modulus show that lower TOC Barnett shale zones show more brittleness. It indicates that these areas are prone for hydraulic fracturing. Seismic inversion is carried out to get the acoustic impedance volume. High AI (low TOC) and low AI (high TOC) areas have been mapped in the survey area.

5.2 Introduction

Shales act as a source rock, reservoir and seal for the oil and gas. In recent years, the production of natural gas and oil from unconventional shale reservoirs has been increased significantly (Montgomery et al., 2005). Barnett shale of Fort Worth basin is one of the early explored shale gas reservoirs in USA. The Barnett shale holds recoverable gas of around 39 tcfg (Powell, 2008). Gas in the shale is mainly stored in three states: (1) as free gas in natural fractures and interparticle porosity (2) as adsorbed gas on kerogen and clay particles and (3) as gas dissolved in kerogen and bitumen (Passey et al., 2012). The key factors in shale gas reservoirs are: (1) reservoir thickness (2) total organic carbon (3) thermal maturity (4) volume of gas in place and (5) amount of adsorbed gas (Bruner and Smosna, 2011).

5.3 Geological setting

The Mississippian Barnett shale is located in the Fort Worth basin in north-central Texas. Geographic limits of the Barnett shale include the Ouachita thrust front to the east, the Muenster and Red river arches to the north, and the eastern shelf and the Concho arch to the west (Montgomery et al., 2005). The Fort Worth basin is formed during the late Paleozoic Ouachita orogeny, generated by convergence of Laurussia and Gondwana land. The north-south structural axis of the basin lies parallel to the Ouachita thrust front (Montgomery et al., 2005). Figure 5.1 shows location of Fort Worth basin.

The Barnett shale is a dense, organic-rich, soft, thin-bedded, petroliferous, fossiliferous shale (Lancaster et al., 1993). The Forestburg limestone which divides the Barnett shale in the northern part of the basin is absent in the southern part of the basin in the study area (Montgomery et al., 2005). Here, Barnett shale is treated as a single,

undifferentiated formation (Figure 5.2). The Barnett unconformably overlies Ordovician carbonate rocks. In the study area, the Barnett shale is overlain by Lower Ordovician Ellenburger group that is comprised of porous limestone and dolomite with abundant chert. Figure 5.2 shows the subsurface structural section of the study area in the Hamilton county, Texas.



Figure 5.1: Location map of Fort Worth basin in USA (EIA, 2014)



Figure 5.2: The north-south stratigraphic section of Fort Worth basin highlighting the Hamilton County (Modified after Montgomery et al., 2005).

The Barnett shale consists of black siliceous shale, limestone and minor dolomite (Montgomery et al., 2005; Loucks and Ruppel, 2007). The average mineralogical composition of Barnett shale is shown in Table 5.1.

Mineral	Percentage
Quartz	35-50
Clays (illite)	10-50
Calcite, dolomite	0-30
Feldspars	7
Pyrite	5
Phosphate, gypsum	trace

Table 5.1: Mineralogical composition of the Barnett shale (Montgomery et al., 2005).

5.4 TOC and maturity

The total organic carbon (TOC) content by weight in the Barnett shale is reported to average 3.16-3.26% (Jarvie et al., 2007). The outcrop samples near Llano uplift have TOC from 11-13% and immature. The kerogen is type II and has the hydrogen index (HI) of 350-475 milligrams hydrocarbon per gram of TOC (Jarvie et al., 2007). The study area has the vitrinite reflectance values between 1.1-1.3 indicating the late matured stage of kerogen. The Barnett shale is in the wet gas window in this area. Figure 5.3 is extracted from Jarvie et al. (2007). Figure 5.3a shows the ternary diagram with average mineralogical composition of Barnett shale and Figure 5.3b shows how the gas flow and brittleness index changes with thermal maturity of Barnett shale. The gas flow increases as the maturity increases.



Figure 5.3: (a) Ternary diagram showing the average mineralogy for Barnett shale (b) The plot showing the relationship between thermal maturity, gas flow and brittleness (From Jarvie et al., 2007).

5.5 Study area

The study area is located in the Hamilton County in Texas (Figure 5.4). The vitrinite reflectance (Ro) ranges from 1.1-1.3 in the area indicating that the Barnett shale

is in wet gas window. The study area has around 140 sq miles of 3D seismic survey. A total of 3 wells have been studied. Mesquite#1 well do not fall in the seismic survey area. The location of the study area with seismic survey is shown in the Figure 5.4.



Figure 5.4: (a) Map showing the maturity level (Ro) of the Barnett shale in Fort Worth basin (Modified after Montgomery et al., 2005). (b) The zoomed view of the study area in Hamilton county.

Figure 5.5 is a SEM image of the Barnett shale in the well Mesquite#1. The layered structure of the clay platelets is clear from the image.



Figure 5.5: SEM image from the core from the well Mesquite#1 (Image courtesy from Marathonoil).

5.6 Delta log R technique

Visual analysis for organic content is based on the porosity-resistivity overlay technique (Passey et al., 1990), used to locate possible hydrocarbon shows in log analysis. By extending this method to radioactive zones like shales, we can identify potential source rocks, gas shales and oil shales. Usually the sonic log is used as porosity indicator (Passey et al., 1990), but neutron or density log also be used (Bowman, 2010).

Delta log R technique (Passey et al., 1990; Meyer and Nederlof, 1984; Bowman, 2010) is used to identify source and non-source rocks. The trick is to align the sonic log on top of the logarithmic scale resistivity log so that the sonic curve lies on top of the resistivity curve in the low resistivity shales. Low resistive shales are non-source rocks. Shales or silts with source rock potential show considerable crossover between sonic and resistivity logs. The absolute value of the sonic and resistivity in the low resistivity shales is called base-lines, and these lines vary with depth of burial and geological age (Passey et al., 1990).

TOC in Barnett shale from the producing area varies from 0.4 to 10.6%, with an average of 4.0% (Loucks and Ruppel, 2007). Figure 5.6 shows the well logs of Mesquite#1. TOC log generated using Delta log R technique is shown on the right track. The TOC measurements done in the lab on the core samples is also shown. It is evident that we got good correlation between predicted TOC log and lab TOC measurements. A crossover is also observed between Vp and Deep resistivity logs as shown in the track 4. This crossover may be an indicator of shale maturity.



Figure 5.6: Well logs of the well Mesquite#1. TOC log predicted from Delta log R technique is shown on the right track (track 5).

5.7 Rock properties from well logs

It is important to understand the relationship between rock properties such as porosity and seismic properties such as acoustic impedance at the wells. We can achieve it using well logs. Here, we looked at the relationship between rock property, TOC and seismic property, P-impedance in the Barnett shale zone for the well Mesquite#1 (Figure 5.7). P-impedance log is a resultant of product of P-wave velocity and bulk density logs. The total thickness of the interval is around 110ft. It is color coded with depth.



TOC (wt%) in fraction

Figure 5.7: The relationship between TOC and P-impedance in the Barnett shale zone for the well Mesquite#1.

Figure 5.8 shows the relationship between P-impedance and Young's modulus (E) in Barnett shale zone for well Mesquite#1. E can be calculated from Vp, Vs and bulk density using the following relationship.

$$E = \{\rho V s^2 (3V p^2 - 4V s^2)\} / \{V p^2 - V s^2\}$$
(1)

The plot is color coded with TOC. We know that high P-impedance and high Young's modulus shale behave as more brittle and lower values of both behave as more ductile. It is clear from the plot that lower TOC Barnett shale zone has more brittleness than the higher TOC zone. So, the lower TOC zone is more suitable for hydraulic fracturing for better hydrocarbon production.



Young's modulus (GPa)

Figure 5.8: The relationship between P-impedance and Young's modulus for Barnett shale zone in the well Mesquite#1.

Figure 5.9 shows the composite well log with inserted seismic traces along the well Duncan Ranch#1P.



Figure 5.9: The composite well log plot for well Duncan Ranch#1P

5.8 Acoustic impedance inversion

Seismic inversion is the process of transforming seismic reflection data into a quantitative rock property description of a reservoir (Wikipedia). Acoustic impedance is a layer property, whereas seismic data is an interface property. Seismic inversion integrates data from various disciplines and domains (well data in depth, seismic interpretation and amplitudes usually in time). Inversion on the stacked data always useful as it is associated with minimum noise.

In the seismic method, we get reflections from the subsurface rock layers. We convolve the reflections with different wavelets. After summation, we finally get the seismic trace which also contains noise (Figure 5.10). Seismic inversion is the reverse of the seismic method. It starts with seismic trace and finally gets the impedance. The key part in seismic inversion is estimating the wavelet and removing its effect. A model based acoustic impedance inversion is carried out using Hampson-Russell's STRATA software package.



Figure 5.10: Schematic showing the seismic method and seismic inversion

The model-based acoustic impedance inversion is an integrated approach from well data such as sonic, density logs, markers, and major interpreted horizons and poststack seismic data. The workflow for model based impedance inversion is shown in the Figure 5.11. The wavelet is estimated from the wells Duncan Ranch#1P and Lake Davis#1P along the time window from 500-800ms.

Seismic is a band limited data i.e., it has certain frequencies only. The lower and upper frequencies miss from the recorded seismic data. The missing low frequencies are added from the sonic logs of these two wells. Figure 5.12 shows the low frequency model from seismic and well log data.

Finally, we invert the seismic data to get the impedance inversion result. As we are using P-wave reflection data (zero degree offset), it is termed as P-impedance or acoustic impedance data. This data is a resultant of both porosity and lithology.



Figure 5.11: Typical workflow for model based acoustic impedance inversion



Figure 5.12: Schematic showing the low frequency model



Figure 5.13: Acoustic impedance section along well Duncan Ranch#1P with TOC log inserted

The acoustic impedance section along the well Duncan Ranch#1P is shown in the Figure 5.13. TOC log is inserted along the well bore. Top of the Barnett shale is demarcated on the section. Barnett shale reservoir zone is having low impedance than the underlying Ellenberger limestone.

Figure 5.14 shows the same acoustic impedance section along the well Duncan Ranch#1P with Gamma Ray curve is inserted.



Figure 5.14: Acoustic impedance section along well Duncan Ranch#1P with Gamma Ray log inserted

A horizon slice is extracted 10 ms below the top of the Barnett shale horizon and is shown in the Figure 5.15. The lighter colors show lower acoustic impedance and dark colors show high acoustic impedance values. As we observed from the well log analysis that lower acoustic impedance corresponds to high TOC, it can be inferred here that the low AI area shown on the map has high amount of TOC in the Barnett shale. But, from

the Figure 5.8, we found that lower TOC shale zone is showing more brittleness and these zones play an important role in production.



Figure 5.15: Map of the horizon slice extracted 10ms below the top of the Barnett shale

5.9 Conclusions

Good correspondence is found between the TOC log generated from sonic and resistivity logs with the core measurements. The crossplots between TOC and AI (Acoustic Impedance) from the well logs indicate that both of them have an inverse relationship. Crossplot analysis show that lower TOC Barnett shale zones show more brittleness. It indicates that these areas are suitable for hydraulic fracturing.

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Chapter 6

Anisotropy and micro-structural characterization of Green River shale

6.1 Abstract

The anisotropy of Green River shale outcrop samples is measured by me in the rock physics lab at the University of Houston. Elastic constants and Thomsen anisotropic parameters are derived from the ultrasonic measurements. We observed both positive and negative values for Thomsen's anisotropic parameter, δ . The peculiar behavior of δ is investigated. AVO and forward seismic modeling results show the different characteristics of seismic properties between source and non-source shale rocks.

A detailed knowledge of microstructure properties helps us to understand the pore connectivity, fluid mobility, which is critical in successful characterization of unconventional shale reservoirs. We used GSA (Generalized Singular Approximation) method to determine the microstructure such as pore/crack shape, and their connectivity for the same samples. The optimized anisotropic microstructure properties can be obtained from solving an inverse problem of GSA modeling, by minimizing the objective function, which is defined as the difference of anisotropic P and S velocities between ultrasonic measurements and the GSA calculation.

6.2 Introduction

Seismic and petrophysical properties of shales and the relationships among these properties are important for both exploration and reservoir management. Shale reservoir characterization from seismic is still a big challenge for geoscientists. In this chapter, I discussed about the ultrasonic measurements and used them in the forward seismic modeling to better characterize the shale reservoir, and also used GSA (Generalized Singularity Approximation) for microstructural characterization from lab measurements.

6.3 Ultrasonic measurements for shale anisotropy

A material is anisotropic if the value of a vector measurement of a rock property varies with direction. Anisotropy is a common phenomenon cutting across diverse disciplines of petroleum industry. Different disciplines of oil industry treat anisotropy in different ways. Geophysicists generally focus on variation of seismic wavefront velocity or on the polarization of shear waves. Anisotropy in sediments may develop during deposition or post deposition. The main causes of elastic anisotropy in shales appear to be layering of clay platelets on the micron scale due to geotropism – turning in the earth's gravity field – and compaction enhances the effect. The other factors for shale anisotropy may include mineralogy, micro-cracks, and organic matter.

An outcrop rock of Green River shale is collected from Green River basin, Wyoming, USA. The sample location is shown in the Figure 5.1. The rock is cored into three different plugs at 0^0 , 45^0 , and 90^0 and the petrophysical properties such as mineralogy, grain density and porosity of each plug is measured by me in the rock physics laboratory at the University of Houston (Figure 6.1). For a transversely isotropic (TI) rock, three plugs must be measured separately, one parallel, one perpendicular, and one at 45 degree to the symmetry axis in order to derive the five independent elastic constants (Vernik, 1994).





The velocities and densities measured on these core plugs yield the elastic constants C_{33} and C_{44} , C_{13} , C_{11} , and C_{66} . The advantage of this three-plug method is redundancy for calculations of the five independent elastic constants since each core plug measurement yields three velocities (one P and two S).

Ultrasonic measurements are made using pulse transmission method (Sondergeld et al., 2000). The measurements were made initially on the dry samples and the same samples are saturated with brine (specific gravity is about 1 g/cc) for couple of days and again measured the velocities. The pore pressure is kept at atmospheric pressure so that the confining pressure equals to effective pressure. Figure 6.2 shows the effect of pressure on velocities for both dry and saturated samples. P-wave anisotropy is around 15-17% and S-wave anisotropy is around 20-22%. And also, the velocities are increasing with effective pressure due to the closure of microcracks in the rock samples.

The elastic constants are calculated using the velocity and density values and the variation of these constants with the pressure are shown in the Figure 6.3. It is observed from the plots that C_{11} and C_{33} are sensitive to pressure.


Figure 6.2: Effect of pressure on velocities for (a) dry and (b) saturated samples



Figure 6.3: Effect of pressure on elastic moduli for (a) dry and (b) saturated samples

The Thomsen anisotropic parameters ε , γ , and δ are calculated from the elastic constants and the variation of these parameters with pressure is shown in the Figure 6.4. The anisotropy parameters ε and γ are decreasing with pressure increase, but the parameter δ has a peculiar behavior. δ shows negative values, the reasons are not known.



Figure 6.4: Anisotropic parameters for dry samples

6.4 Peculiar behavior of δ

Thomsen anisotropic parameter, δ , is important to understand the small offset NMO velocity and vertical velocity, and to interpret the small offset AVO response (Thomsen, 1986). δ is independent of horizontal velocities (Thomsen, 1986). δ has both positive and negative values, for which the physical meaning is not clearly understood. The negative values of δ may be due to the effects of clay particle interaction and disorder in the alignment of clay particles (Sayers, 2005), also the negative values of δ may be due to the error in the coring of 45 degree plug (Sondergeld et al., 2000). And δ is sensitive to velocity measurements.

I calculated the δ using the Thomsen (1986) approximation by considering the same velocity measurements and changing the angle (Figure 6.5). The δ values are positive upto 45 degree and become negative as the angle increases. I calculated δ (for angle 60 degree) using Thomsen (1986) and Berryman (2008) approximations for Vp and Vs (Figure 6.6). It is clear that Thomsen's approximation is negative where as Berryman's

approximation is positive for Vp (Figure 6.6a) and both of them are similar for Vs (Figure 6.6b). I found that $(\varepsilon - \delta)$ is the deciding factor for both Thomsen and Berryman approximations.



Figure 6.5: Thomsen's approximation of δ for different angles



Figure 6.6: Comparison of Thomsen and Berryman's approximations for 60⁰ angle using (a) Vp and (b) Vs

6.5 AVO and forward seismic modeling

A two-layer model is built to understand the seismic properties of the shales. The top layer is assumed to be non-source shale (Vp=3170m/s; Vs=1695m/s; ρ =2.51gr/cc). The second layer is assumed to be source shale reservoir and its velocity and density

values (Vp=2810m/s; Vs=1505m/s; ρ =2.16g/cc) are considered from the lab measurements at 5000 psi pressure.

AVO (Amplitude Variation with Offset) modeling is done for PP and PS reflection amplitudes using Shuey's two term approximation (Castagna and Swan, 1997). The reflection amplitude of PP is decreasing as the offset increases, showing a typical class II AVO (Figure 6.7). The PS reflection amplitude increase from 10-45 degrees and then gradually decreases from 45-90 degrees. The forward seismic modeling for PP and PS reflectivity modeling are shown in the Figure 6.8. NMO corrected gathers and stacks are shown. The amplitude of the PS reflectivity is increasing from near to far offset.



Figure 6.7: AVO plots for (a) PP and (b) PS reflections



Figure 6.8: NMO removed and stack gathers for (a) PP reflectivity and (b) PS reflectivity modeling

6.6 Generalized Singularity Approximation (GSA) method

One of the major challenges to characterize the shale reservoirs is to get the microstructure information, i.e., the clay platelet orientation, the type, density, shape, and connectivity of the inclusions. These are directly linked to three physical parameters: porosity, aspect ratio, and friability with the assumption that the pore/cracks are gas-filled and have ellipsoidal shape.

The problem of calculating the effective stiffness tensor is a many-body problem, which can be solved, in general case, only approximately (Chesnokov et al. 1995). The majority of the methods of effective medium theory is based on the Eshelby (1957) solution, which finds the strain field in an individual ellipsoidal inclusion embedded in a homogeneous matrix with other elastic properties, caused by a stress (or strain) field applied at infinity. In the effective medium theory, it is assumed that the inclusions (mineral grains, pores and cracks) have an ellipsoidal shape. Hornby et al. (1994) used biconnected clay matrix cracks in isotropic clay matrix and rotated them in accordance with the distribution function of the clay platelet orientation. Then, silt-sized minerals were inserted resulting the anisotropic 'clay-cracks' material.

We used GSA method to compute the effective elastic constants of cracked anisotropic media for arbitrary crack concentration and aspect ratio. We consider that clay forms a matrix containing grains of different minerals, pores and cracks with different shape and orientation as inclusions. This consideration is in line with the microstructure seen in SEM (Scanning Electron Microscope) image shown in Figure 6.9.



Figure 6.9: SEM image of a shale microstructure

GSA (Shermergor, 1977) uses the singular part of Green's function to get the analytic solution. GSA is a powerful effective medium modeling method for porous

media. It gives the effective properties of the whole medium provided the components of the rock (i.e., matrix and inclusions). The advantages of GSA over other EMT (Effective Medium Theory) models are: GSA can handle large volume of inclusions, it takes into account the effect of the connection of pores, it works for arbitrary ellipsoidal inclusion with any aspect ratios, it assumes that the elastic properties are anisotropic for both matrix and inclusions.

According to Hooke's law, the effective stiffness tensor is related via strain (ϵ) and stress (σ) fields averaged over a representative volume:

$$<_{\sigma}> = C^* <_{\varepsilon}> \tag{1}$$

The derivation is based on a comparison of the displacement fields arising in the heterogeneous body whose effective properties have to be found in a homogeneous reference body. The stiffness tensors of heterogeneous body and homogeneous reference body are represented by C and C^c respectively.

In the GSA method, the choice of reference body is arbitrary. If a two-component body is considered (as porous cracked medium), the choice of reference body as mineral matrix, gives the upper Hashin-Shtrikman bound (isolated fluid inclusion and continuous mineral matrix), the choice of reference body as fluid inclusions gives the lower Hashin-Shtrikman lower bound (continuous fluid phase and isolated solid inclusions).

Figure 6.10 shows the workflow for the GSA modeling and inversion for microstructural characterization.

Bayuk and Chesnokov (1998) used the stiffness tensor of the reference body for a porous cracked medium in the form of a combination of matrix and fluid stiffness tensors as $C^{c} = (1-f) C^{m} + f C^{fl}$ (2)

Here the indices m and fl are matrix and fluid respectively. The coefficient f is called the friability, which is an empirical coefficient that to some degree reflects pore/crack connectivity.



Figure 6.10: The workflow for GSA method

6.7 GSA modeling and inversion for microstructure

GSA method is used for microstructure characterization of Green River shale samples. It involves two steps. In the first step, modeling is carried out only for minerals. It treats clay minerals as matrix and other minerals such as quartz, calcite, dolomite, feldspar as inclusion. It uses the matrix property as comparison body, because friability of the inclusion of granular minerals is zero i.e. isolated. The velocities at different angles (0, 45, and 90) are calculated using Green-Christoffel equation. These velocities are then compared with the ultrasonic velocities for the same angles.

In the second step, inversion is carried out which includes pores/cracks. It uses the GSA result from pure minerals as matrix and adds gas-filled pore/cracks as inclusions. Finally, we get the following microstructural properties from the inversion: 1. Porosity 2. Aspect ratio of cracks (χ) and 3. Friability (f). A global search algorithm is applied for the range of above parameters to minimize the objective function. Figure 6.11 shows the schematic for the microstructure properties from GSA modeling and inversion.



Figure 6.11: Schematic of the GSA method for microstructure characterization

GSA modeling for the Green River shale is carried out using the mineral composition measured by FTIR, the elastic constants and densities taken from published literature. The velocities calculated and measured from ultrasonic are plotted for the three plugs and shown in the Figure 6.12. The difference between the velocities is due to only the mineral matrix is considered.

In the Figure 6.12, circle, square and plus points denote the ultrasonic velocity measurements of 0, 45 and 90 degree samples in laboratory, and line curves denote the

GSA modeling result for the pure solid mineral composite without any porosity. The density of mineral composite is 2.69 g/cc.



Figure 6.12: P, S1 and S2 velocities with different incident angles calculated from GSA modeling of pure mineral composite.

P, S1 and S2 velocities with different incident angles calculated from GSA modeling of the whole shale sample with full consideration of mineralogy, porosity, pore/crack aspect ratio and friability, where the aspect ratio and friability are obtained from GSA inversion in order to make best agreement between velocities from laboratory measurement and from the GSA modeling results (Figure 6.13). Circle, square and plus points denote the ultrasonic velocity measurements of 0, 45 and 90 degree samples in laboratory, and line curves denote the GSA modeling result for the whole shale sample with optimal aspect ratio and connectivity of pore/cracks. The average density of the shale samples is 1.883 g/cc.



Figure 6.13: Comparison of calculated and experimental velocities after inversion.

From the inversion result, the aspect ratio (χ) is estimated around 0.9046, which infers that the shape of the fluid inclusions is almost spherical. The friability (f), which indicates the connectivity between inclusions, is estimated around 0.9057. The range of friability is between 0 and 1, where 0 is considered as no connection and 1 is considered as well connected among the inclusions. So, the calculated friability from the inversion indicates that there is a good connection between the inclusions.

6.8 Conclusions

The ultrasonic measurements on the Green River shale show that it is anisotropic in nature. The calculation of δ is ambiguous as different approximations yield different values. AVO modeling shows typical class II AVO for the source shale reservoir. The seismic forward modeling results show the distinctive seismic properties for source and non-source shale rocks.

We used GSA method for microstructural characterization of Green River shale samples. One of the major advantages of GSA over other methods is that we can estimate the connectivity between pores/cracks (friability). The inversion results show that the pores have spherical shape and are well connected. The reason for the difference in the velocities between calculated and measured in the lab is due to changes in the pressure and temperature conditions while measuring the elastic moduli of the minerals. The elastic moduli of each mineral are considered from the published literature, so the conditions may not be the same for the each mineral, which contributes to the mis-match between the inversion and ultrasonic results.

6.9 References

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Chapter 7

Concluding remarks and Recommendations

7.1 Concluding remarks

The dissertation work shows that the hydrocarbon-induced cracks generated during kerogen maturation do not produce much of an effect on the seismic anisotropy after compaction. The analysis from published data indicates that the seismic properties (velocities and anisotropy) are affected by the level of kerogen maturity.

Over-pressure caused by kerogen transformation of oil/gas affects the seismic properties. AVO and wave propagation are also affected by over pressure.

From the rock property analysis for Barnett shale, we observed that the high TOC shale zones have lower acoustic impedance. And lower TOC zones are more brittle and suitable for hydraulic fracturing.

7.2 Recommendations

1. During anhydrous pyrolysis, the sample was heated only for 3 days. It would be interesting to heat the sample for more time with different temperatures. It would also be a good idea to heat the sample for 100 C for a week; subsequently, to carry out a microstructural analysis; as well as to gather ultrasonic measurements;

furthermore, to repeat the same process at different temperatures like 200 C, 300 C. This process would provide insight into how the micro-structure and the elastic properties are changing in relation to the temperature (maturation).

- 2. For the purposes of this dissertation, type I kerogen shales were used. It would be interesting to see and understand how the micro-structure and elastic properties might change other kerogen shales with artificial maturation, as well as to learn whether the type of kerogen has any effect on elastic properties.
- **3.** Simultaneous measurement of ultrasonic velocities while heating the sample for higher temperatures would be recommended. However, the challenge is manufacturing acoustic transducers that can withstand high temperatures.
- **4.** The elastic properties of bitumen are also very important and useful for rock physics analysis.