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Property Changes of Oil Shale During Artificial Maturation: the Irati Formation from the Paraná Basin, Brazil

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Running head: Maturation of Irati Oil Shale

ABSTRACT

Acquiring elastic property information from oil shale during pyrolysis remains a difficult endeavor. We subjected oil shale samples from the Irati Formation in the Paraná Basin, Brazil to high-temperature, high-pressure hydrous and anhydrous pyrolysis while simultaneously acquiring compressional and shear waveform data. We present elastic properties as a function of temperature at constant differential pressure using samples cored in three different
directions relative to the bedding plane. Hydrous pyrolysis decreased total organic carbon (TOC) in samples from 25 to 20 wt%, while anhydrous pyrolysis had no significant change in TOC. The cores experienced higher strain hysteresis (up to \(-0.094\) residual axial strain) after hydrous pyrolysis compared to after anhydrous pyrolysis (\(-0.56\) residual axial strain). The larger residual strain was accompanied by a larger increase in shear velocity up to 35% after hydrous pyrolysis as compared to the 3% shear velocity increase after anhydrous pyrolysis. The change could be a result of compression and loss of organic content determined at ambient temperature 25°C. We quantified sample changes using x-ray computed tomography (CT), scanning electron microscopy (SEM), source rock analysis, and x-ray diffraction (XRD) before and after pyrolysis. Our data on elastic properties and Thomsen’s parameters during pyrolysis can be used to extract material property information useful for improving subsurface well logging and 4D seismic to produce efficiently from oil shale formations.
INTRODUCTION

Measuring acoustic and mineralogical properties of oil shale before and after pyrolysis can characterize the effectiveness of oil shale production. However, acoustic properties measured before and after pyrolysis do not adequately characterize the changes in oil shale seismic properties during in-situ maturation. Most studies have evaluated the effects of artificially induced thermal maturation on organic-rich shale at ambient (room temperature) laboratory conditions (Prasad et al., 2011; Lewan and Roy, 2011; Hu, 2012; Lewan et al., 2013; Allan et al., 2014; Patrusheva et al., 2014; Yenugu, 2014; Spigolon et al., 2015; Zargari et al., 2016), as a function of pressure (Vanorio et al., 2008; Yan et al., 2012; Allan et al., 2013), or as a function of varying clay and organic contents (Vernik and Liu, 1997; Qin et al., 2014). Few studies have evaluated oil shale seismic property changes during high-temperature, high-pressure experiments (Mraz et al., 1983; Behura et al., 2009; Baharia et al., 2011; El-baharia, 2012; Uvarova et al., 2014). We acquired shear and compressional waveforms while conducting anhydrous and hydrous pyrolysis experiments on oil shale samples from the Irati Formation in the Paraná Basin, Brazil, and evaluated this data along with mineralogical, petrographical, and geochemical properties of the samples before and after pyrolysis.

Upper Permian Irati oil shale typically contains immature type I kerogen (Da Silva and Cornford, 1985; Zalan et al., 1990), and at temperatures of several hundred degrees Celsius, the organic matter (kerogen) can decompose to produce oil and gas (Dyni, 2006). Two types of commercial scale production from oil shale include: 1) in-situ retorting and 2) aboveground retorting (Qian and Wang, 2006). Current successful production methods of Irati oil shale utilize the aboveground retort system known as Petrosix (Yenugu, 2014). Aboveground retorting is not only costly, but generates considerable waste (Xuehui and
Jinming, 2009). Therefore economically viable in-situ production is of great interest. The 4D seismic data and attribute analysis based on elastic moduli (Li and Zhao, 2014) could characterize the oil shale formation and help optimize in-situ production. However, changes in anisotropy (characterized by changes in Thomsen’s parameters) need to be accounted for to correctly process seismic data of oil shale formations during production, using methods described in Simm and Bacon (2014).

Lewan and Roy (2011) and Lewan et al. (2013) suggest that hydrous pyrolysis results in better hydrocarbon and petroleum formation. Lewan and Roy (2011) find that hydrous pyrolysis of Mahogany oil shale (which contains type I kerogen) results in 29% more petroleum, while anhydrous pyrolysis shows a lack of thermal cracking and lower total organic carbon (TOC) change compared to hydrous pyrolysis. Additionally, hydrous pyrolysis at 350°C for 72 hours has a greater effect on bitumen decomposition into oil than the kerogen to bitumen conversion at 330°C. For production purposes, hydrous pyrolysis needs to be implemented at higher temperatures and heating rates. Uvarova et al. (2014) observes significant fracturing of Kimmeridge shale during hydrous pyrolysis at temperatures above 390°C and heating rates of 8°C/min. While acquiring acoustic data during hydrous pyrolysis is desirable, sample degradation presents a challenge for reliable data acquisition. Therefore, we limit the heating rate, maximum temperature, and hold time to 10°C/10min, 365°C, and 48 hours, respectively.

Lewan and Roy (2011) recommend pressures in excess of 13 MPa at temperatures of 350°C for optimum production, but also note that these pressures and temperatures are difficult to maintain at the shallower depths of oil shale formations. Furthermore, Allan et al. (2013) show an increase in P-wave anisotropy of oil shale samples as a function of differential pressure after anhydrous pyrolysis, with anisotropy changes appearing at
10 MPa. Therefore, to compare the effects of hydrous and anhydrous pyrolysis on our Irati samples without added ambiguity from pressure-dependent anisotropy, and taking into consideration the typically shallow depths of the Irati formation (Zalan et al., 1990), we keep our samples under a constant differential pressure of 800 psi (approximately 5.5 MPa).

The ability to collect acoustic waveform data during hydrous pyrolysis provides valuable insight into the changes occurring in the rock properties. Baharia et al. (2011) proposes a process for acquiring acoustic data on oil shale samples as a function of temperature at constant pressure during anhydrous pyrolysis. Using this process, we measure acoustic properties of Irati oil shale core samples while subjecting them to anhydrous and hydrous pyrolysis. In order to understand the driving mechanisms for changes observed in the data derived from the acoustic waveforms, we utilize x-ray computed tomography (CT), scanning electron microscope (SEM) images, source rock analysis, and x-ray diffraction (XRD) mineralogy data. To our knowledge, no other data set exists that collects acoustic waveforms during hydrous pyrolysis.

METHODS

A total of six core plugs, each 1 in. diameter by 1 in. length, were used for pyrolysis experiments: three for hydrous pyrolysis, and three for anhydrous pyrolysis. Each of the three plugs were cored at different orientations with respect to the symmetry axis (0°, 45°, and 90°, as depicted in Figure 1). An additional seventh core plug cored at 0° to the symmetry axis was subjected to the ramp-up phase of hydrous pyrolysis as a calibration experiment. Before performing pyrolysis experiments, we characterized the mineralogical, petrographical, and geochemical properties of the samples. CT scans confirmed that we
had cored samples to the desired orientation and quantified deformation after pyrolysis. SEM images showed detailed sample surfaces and provided qualitative pore information. Separate aliquots adjacent to where the core plugs were drilled were analyzed using source rock analysis and XRD to determine the maturity and the mineralogical constituents of the oil shale, respectively. After the pyrolysis experiment, we again collected CT, SEM, source rock analysis, and XRD data from the samples. Samples for SRA and XRD were a mixture of aliquots taken from each of the three differently oriented core plugs after anhydrous pyrolysis, and the same procedure was followed after hydrous pyrolysis. This information allows us to compare results before, during, and after pyrolysis, and provide explanations for the observed trends of the acoustic data.

**High-temperature, high-pressure experiment**

Figures ?? and 3 show the setup and temperature steps, respectively, for the pyrolysis method that was used (Gayer, 2015). For each experiment, we placed a core sample inside a flexible, stainless steel confining jacket and axially bound it with lithium niobate transducers that operated at a frequency of 1 MHz (Figure 4), based on methods in Baharia et al. (2011). Confining pressure was applied from nitrogen gas, and internal pore pressure was applied from either nitrogen gas for anhydrous pyrolysis, or brine for hydrous pyrolysis. We wrapped a heating element around the confining jacket and thermocouples, and placed the entire assembly into the high-temperature, high-pressure vessel. Nitrogen gas was applied to reach the initial confining pressure of 1000 psi. Pore pressure of 200 psi was applied using either nitrogen for anhydrous pyrolysis or 100,000 ppm NaCl brine solution for hydrous pyrolysis.
Pressures were chosen to: 1) simulate shallow in-situ conditions of the Irati Formation at depths of approximately 3200 m (Espitalié et al., 1983; Zalan et al., 1990); 2) avoid velocity changes associated with higher confining pressures, as observed by Allan et al. (2013); and 3) keep consistent coupling between the transducers and the core sample. We conducted two types of pyrolysis experiments. In one (the anhydrous experiment), we increased confining pressure at 20 psi/min up to 1000 psi using dry nitrogen gas, and then increased pore pressure at 20 psi/min up to 200 psi. In another (the hydrous experiment), we increased confining pressure at 20 psi/min up to 1000 psi using dry nitrogen gas, and increased pore pressure in 20 psi steps up to 200 psi using a 100,000 ppm NaCl solution. In both hydrous and anhydrous experiments, the differential pressure (confining pressure - pore pressure) was maintained at 800 psi. The high salinity brine solution was intended to counteract any effects of clay swelling in the samples, as well as emulate high salinity in shale formations, such as the Bakken, which has brine salinity up to 280,000 ppm (Faybishenko et al., 2015).

The temperature of a sample started at 25°C, and then increased by 10°C every 10 minutes, until reaching 365°C (ramp-up phase). The temperature was kept at 365°C for 48 hours. Then, the temperature was lowered by 10°C every 10 minutes until reaching 25°C (cool-down phase). A heating and cooling rate of 10°C/10 minutes was implemented to prevent sample deformation as temperature changed, because significant strain in samples occurs at high temperatures during hydrous pyrolysis (Lewan and Roy, 2011); a parallel calibration experiment was run to verify that no strain occurred in the samples during the ramp-up and cool-down phases. Samples were held at 365°C for 48 hours to have maximum oil generation (Lewan and Roy, 2011). Samples were also held at temperatures of 365°C to simulate in-situ production proposed by Shell Exploration and Production (Boak, 2007).

We collected compressional and shear waveforms at each temperature step and maintained
approximately 800 psi differential pressure throughout the experiments.

**Waveform collection and velocity analysis**

Waveforms were recorded with a storage oscilloscope and digitized with 10,000 points. Velocities were calculated from first arrivals of each wave type in the stored waveforms. Figure 5 provides an overview of the velocity determination process. First arrivals of compressional waves (Figure 5a) were easier to detect since they were the primary waves to be recorded. Identification of first arrival of shear waves (Figure 5b) was more difficult due to compressional wave pre-cursors. Shear waves arrived later than compressional velocities, and had a longer transducer delay time. Therefore, first arrival picking of shear waves were based on the largest waveform amplitude that did not coincide with the compressional wave first arrival picks.

To verify that sample lengths did not compress or expand significantly during the ramp-up or cool-down phase of the pyrolysis experiments, we performed an additional calibration experiment: We measured the length of a separate sample (cored at 0°), and subjected it to the ramp-up phase of hydrous pyrolysis. We used a sample with 0° orientation because that orientation is most susceptible to potential axial strain in these conditions. After samples reached 365°C, we immediately turned off the heating element, quickly cooling the sample. We again measured the length, and determined that no strain occurred. We could then assume that each of the other six core samples had consistent lengths during the ramp-up and cool-down phases. We determined the velocities by dividing the known lengths by the picked arrival time in the waveforms. Due to the unknown rate of sample strain occurring during the 48-hour period at 365°C, we could not accurately determine the velocities during
this time.

Stiffness coefficients were calculated based on interpreted velocities and densities of the individual samples, after King (1964). From these velocities, densities, and stiffness coefficients, and using the assumption that our samples have vertical transverse isotropy (VTI), we derived elastic moduli (bulk modulus and shear modulus), Poisson’s ratio, and Thomsen’s parameters as a function of temperature, using relationships from Thomsen (1986). Elastic moduli are useful for relating geophysical data and petrophysical properties (Aminzadeh and Dasgupta, 2013), and Thomsen’s parameters are useful for characterizing wave propagation in weakly anisotropic media (Grechka et al., 2011).

Equations for Thomsen’s parameters are shown in equations 1-3. Parameters $C_{11}$ and $C_{33}$ define the stiffness coefficients derived from the horizontal (axes 1 and 2) and vertical (axis 3) compressional velocities, respectively, while $C_{66}$ and $C_{44}$ define the stiffness coefficients derived from the horizontal and vertical shear velocities, respectively. Therefore $\varepsilon$ (equation 1) is the fractional difference in vertical and horizontal compressional wave velocities, and $\gamma$ (equation 2) is the fractional difference in vertical and horizontal shear wave velocities (Thomsen, 1986). The third Thomsen parameter, $\delta$ (equation 3), controls the near-vertical anisotropy, and has no dependence on the horizontal compressional velocity (Thomsen, 1986):

$$\varepsilon = \frac{C_{11} - C_{33}}{2C_{33}},$$

(1)

$$\gamma = \frac{C_{66} - C_{44}}{2C_{44}},$$

(2)
\[ \delta = \frac{(C_{13} + C_{44})^2 - (C_{33} - C_{44})^2}{2C_{33}(C_{33} - C_{44})}. \] (3)

**Computer tomography**

To ensure accurate symmetry orientation\(^1\) of core samples and to identify fractures, we collected CT scans on each of the six samples before and after pyrolysis. We used an Xradia-400 micro CT scanner to observe the samples at approximately maximum field of view (2 in. by 2 in.), resulting in an approximate resolution of 70 \(\mu m\) (Schindler and Prasad, 2016). Using CT scans and caliper measurements, we recorded the height and diameter in four locations for each of the six samples before and after pyrolysis to determine the strain.

**Scanning electron microscope**

To determine a qualitative analysis of pore size and hydrocarbon generation and to get high resolution images of the oil shale samples, we utilized two different scanning electron microscopes (SEM) on samples: 1) an environmental scanning electron microscope (ESEM); and 2) a field emission scanning electron microscope (FESEM). The ESEM is a FEI Quanta 600I Environmental SEM, and the FESEM is a JEOL JSM-700F Field Emission SEM. Images taken with the ESEM and FESEM are between 2.5-3.0 nm and 1.2-1.5 nm in resolution, respectively.

\(^{1}\text{within 1° accuracy}\)
Source rock analysis

Source rock analysis was performed on aliquots from the same block of oil shale as the sets of core samples via a Source Rock Analyzer (SRA, Weatherford Laboratories,®). This provided us with S1, S2, S3, Tmax, and TOC values. The S1 value represents the release of free and adsorbed hydrocarbons (Lafargue et al., 1998; Behar et al., 2001). The S2 value represents convertible hydrocarbon compounds from the existing kerogen (Lafargue et al., 1998; Behar et al., 2001). The S3 value corresponds to the oxygen containing compounds (carbon dioxide and water) released during pyrolysis (Lafargue et al., 1998). The Tmax is the temperature value at which the S2 peak reaches its maximum (Behar et al., 2001).

XRD mineralogy

XRD\textsuperscript{2} mineralogy was performed before pyrolysis, after anhydrous pyrolysis, and after hydrous pyrolysis on aliquots from the same block of oil shale as the core samples. We assume a kerogen conversion factor of 1.25 (type I kerogen) for before pyrolysis and after anhydrous pyrolysis, and 1.20 (type II kerogen) for after hydrous pyrolysis (Tissot and Welte, 1984; Ma and Holditch, 2015). We assumed a kerogen density of approximately 1.14 g/cm\textsuperscript{3} (Hu, 2012). Once the XRD mineral and clay fractions and TOC data (in weight %) were obtained, we determined the kerogen volume fraction, after Vernik (2016). We obtained density measurements of our samples by measuring the mass and volume of the core plugs.

Hydrogen Index (HI) along with Tmax provides information of the origin and type of organic matter (Yenugu, 2014; Zargari et al., 2016). Oxygen Index (OI) indicates the

\textsuperscript{2}accurate to 3 wt% from Weatherford Laboratory measurements
amount of oxygen present in the organic matter, and can also be used to estimate the kerogen type when plotted with the hydrogen index (McCarthyt et al., 2011). The production index (PI) relates the amount of hydrocarbons produced during the first and second stage of SRA heating, $S_1/(S_1+S_2)$, and generally increases with burial depth (McCarthy et al., 2011). An example pyrogram from Weatherford Laboratories from an aliquot of Iriti oil shale sample (as-is) is shown in Figure 6. Samples are heated rapidly to 110°C and held for two minutes. Temperature is then increased to approximately 300°C and held for 4 minutes, after which the temperature increases at a rate of approximately 25°C/min, up to 600°C. We derive the HI, OI, and PI using relationships after Espitalié et al. (1977):

\[
HI = \frac{S_2}{TOC} \times 100 \text{ (mgHC/gTOC),}
\]

\[
OI = \frac{S_3}{TOC} \times 100 \text{ (mgC_2/gTOC),}
\]

\[
PI = \frac{S_1}{(S_1+S_2)}.
\]
RESULTS

We present the results of the CT, source rock analysis, XRD mineralogy, and SEM, before and after pyrolysis. We also present the velocities, and the derived elastic moduli, Poisson’s ratio, and Thomsen’s parameters as a function of temperature during pyrolysis.

Computer tomography results

Pyrolysis caused all six samples to compress in the axial direction and expand in the transverse direction (Table 1). A negative number corresponds to compression, and a positive number corresponds to expansion. All samples decreased in length, and increased in diameter, with the hydrous pyrolysis having up to twice the strain as the anhydrous pyrolysis samples. Samples decreased in length due to the confining pressure from each end of the transducer, and increased in diameter due to the available space in the ribbed section of the confining jacket.

Figure 7 shows the cross-section CT scans of samples at three different orientations before pyrolysis (left column) and after hydrous pyrolysis (right column). In both instances, fractures developed approximately along the bedding plane, and ranged in size from 175 μm to 370 μm. The heating of oil shale converted immature kerogen to bitumen (Boak, 2007), causing the rock to fracture.

Scanning electron microscope results

Figure 8 shows the sample’s surface before pyrolysis using ESEM images. Comparing Figures 8 and 9 show that hydrous pyrolysis had a more significant effect on the oil shale samples than anhydrous pyrolysis. Overall, the sample surface remained the same after
anhydrous pyrolysis, with no visible changes, while the sample surface after hydrous pyrolysis exhibited bitumen generation. The smoothed surface after hydrous pyrolysis can be compared to bitumen coating seen in Zargari et al. (2013). Figure 10 shows an FESEM image of the 90° sample before pyrolysis, with clear presence of quartz, clay, pyrite, and organic matter. We see minimal bitumen flow in the SEM images taken after pyrolysis, but the laminar fracturing shown in Figure 11 indicates evidence of organic matter expansion and loss.

**Source rock analysis results**

Our samples contain type I immature kerogen of lacustrine origin, which is consistent with kerogen found in the Upper Permian Irati oil shale (Da Silva and Cornford, 1985). Source rock analysis results are shown in Table 2. From this data, we plotted Van Krevelan diagrams (Figure 12) to illustrate the change in maturity from before pyrolysis to after pyrolysis. Anhydrous pyrolysis resulted in only a slight reduction of the hydrogen index from 762 to 744 milligrams of hydrocarbons per gram of rock (mgHC/g rock). Hydrous pyrolysis resulted in greater reduction of the hydrogen index, compared to anhydrous pyrolysis, by over 100 mgHC/g rock. The S2 value of these oil shale samples reduced by 70 mgHC/g rock after undergoing hydrous pyrolysis, showing evidence of more mature samples that have potential for liquid oil and gas production compared to the samples that underwent anhydrous pyrolysis.
XRD mineralogy results

Table 3 shows the XRD results for all samples (in weight percent) before pyrolysis, after anhydrous pyrolysis, and after hydrous pyrolysis. We observed less than a 4% difference in XRD data when comparing before pyrolysis to after pyrolysis results. The change in TOC indicates a change in kerogen content, however, and therefore we calculated the kerogen volume percentage (also shown in Table 3). Kerogen volume percentage was roughly twice the TOC weight percentage. The slight increase observed in the kerogen volume percentage was likely due to a lack of observable change after anhydrous pyrolysis. We observed a drop from 51% to 40% in kerogen volume after hydrous pyrolysis, indicating kerogen conversion to bitumen.

Velocity data results

Compressional and shear velocity data from the high-temperature, high-pressure experiment are shown in Figures 13 and 14, respectively. Overall velocities decreased as temperature increased. Anhydrous pyrolysis compressional and shear velocities decreased consistently as a function of temperature, while hydrous had higher variations in the velocity trends. As expected in the case of VTI samples, the 90° sample had the fastest compressional and shear velocities, followed by the 45° and 0° samples. Some sample inhomogeneity is evident by the differences in velocities at 25°C at the start of the experiments between samples with similar bedding orientation.

Hysteresis of the final velocities at ambient temperatures before and after pyrolysis are shown in Table ???. For both anhydrous and hydrous pyrolysis, the compressional velocities increased by less than 11% by the end of the cool-down phase. Shear velocities
at the end of anhydrous pyrolysis had almost no change compared to the beginning (+/−3%), but hydrous shear velocities increased by up to 33%. The discontinuities between velocities (compressional and shear) on the ramp-up and velocities on the cool-down phase at 365°C were most likely caused by the high temperature as well as the brine saturation for the hydrous pyrolysis. Numerical data used to make Figures 13 and 14 are provided in Appendix A, Table 5.

Derived parameters results

Using the velocity data, we derived the bulk modulus, vertical shear modulus, vertical Poisson’s ratio, and Thomsen’s parameters. The bulk modulus (resistance to uniform compression) decreased steadily as temperature increased (Figure 15). The bulk modulus remained consistently higher for samples undergoing anhydrous pyrolysis than for hydrous pyrolysis, with the exception of some erroneous data on the anhydrous ramp-up phase from 155-185°C. The anhydrous pyrolysis bulk modulus values during the cool-down phase stayed higher overall than the anhydrous values during the ramp-up phase. Inversely, the hydrous pyrolysis bulk modulus values during the cool-down phase stayed lower overall than the hydrous values during the ramp-up phase. Note that the hydrous pyrolysis bulk modulus values did not vary much, while the anhydrous bulk modulus ended with an approximate 1 GPa difference.

Figure 16 shows the vertical shear modulus (ratio of shear stress to shear strain in the horizontal directions) decreased as temperature increased. The anhydrous ramp-up and cool-down and the hydrous ramp-up all had very similar shear moduli. As temperature increased, the change in the shear modulus approached 0.5 GPa for anhydrous and hydrous
ramp-up. The hydrous shear modulus on the cool-down phase exhibited a non-linear trend, reflecting the large changes in the shear velocities.

Figure 17 shows the vertical Poisson’s Ratio, or ratio of axial strain to transverse strain in the horizontal direction. During anhydrous pyrolysis, the ratio increased as temperature increases. During hydrous pyrolysis, the ratio decreased slightly as temperature increased. Hydrous pyrolysis therefore results in a higher amount of transverse strain compared to anhydrous pyrolysis.

Thomson’s parameters are shown in Figure 18. The $\epsilon$ Thomson parameter had no noticeable change during anhydrous pyrolysis, and only increased to a maximum of 1.14 during hydrous pyrolysis. The $\gamma$ Thomson parameter increased with increasing temperature during anhydrous pyrolysis, but returned to the same value at 25°C after pyrolysis. A similar trend is observed for $\gamma$ during the hydrous pyrolysis, but the hydrous pyrolysis cool-down phase had a much higher peak of 5.56 at 245°C. This indicates that the shear wave in the axial direction became much faster than the shear wave in the radial direction for a large portion of the cool down phase. The final Thomson parameter, $\delta$, had much greater fluctuation in values during hydrous pyrolysis compared to anhydrous pyrolysis. These results were correlated with other methods (CT, SEM, XRD, and source rock analysis) to explain changes in the waveform derived data in the discussion section.

**DISCUSSION**

First arrivals of compressional and shear waveforms were more difficult to interpret at higher temperatures, especially on the hydrous pyrolysis cool-down phase, for the following reasons:
• The Krytox™ XHIT-BDX couplant used had a maximum operating temperature of approximately 350°C.

• For hydrous pyrolysis in particular, sample deformation during the holding period of 48 hours at 365°C may have damaged the samples and/or further affected the coupling of the transducers to the surface of the samples.

• Sample fracturing or deformation could have lowered the amplitude of the recovered waveform.

We extrapolated some velocity data for the hydrous pyrolysis for temperatures above 325°C until we could recover the waveform data. We picked arrival times of degraded waveforms using cascade plots of the collected waveforms to pick approximate locations, and verified these picks against the most accurate best-fit line. This allowed us to pick velocities even when the waveform quality was significantly degraded. This was done primarily for data missing from the higher temperatures of the cool-down phase of the hydrous pyrolysis. Compressional velocities did not exhibit significant hysteresis. Shear velocities in anhydrous pyrolysis did not change by more than 3%, but shear velocities in hydrous pyrolysis changed by up to 33%. To explain these velocity changes, we examined the other data collected before and after pyrolysis.

Samples that underwent hydrous pyrolysis expanded farther into the ribbed areas of the stainless steel confining jacket, resulting in higher transverse strain. The CT scans show the large fracture that developed during hydrous pyrolysis in the 45°C sample. This likely occurred during the 48 hour period at 365°C, which explains the overall lower compressional velocities on the cool-down phase. During the cool-down phase, as the temperature decreased and the sample remained under confining pressure, pore spaces and fractures
previously filled with air or fluid began to close, resulting in a higher shear modulus. At
approximately 150°C on the cool-down phase of hydrous pyrolysis, the bitumen went below
its glass point and became soft, as expected based on the 30°C-157°C range for soft bitumen
(Drews, 1998). This explains the leveling out of the shear modulus for the remainder of the
hydrous pyrolysis cool-down phase. The decrease in temperature, the closure of fractures,
and the loss of organic matter observed in the source rock analysis and SEM images of
bitumen flow resulted in higher velocities below 150°C on the cool-down phase.

Mineralogy and source rock analysis data verify the change in the organic material
and, therefore, the change in the moduli. Mineralogy composition remained consistent, but
source rock analysis showed a higher increase maturity from hydrous pyrolysis compared to
anhydrous pyrolysis. Using the mineralogy and the TOC values before and after hydrous
pyrolysis, the Kerogen volume was calculated to be 51% before pyrolysis, and 40% after
hydrous pyrolysis. Kerogen volume remained approximately constant after anhydrous py-
rolysis, but this can be explained by the TOC being approximately equal with the TOC
before pyrolysis.

During the cool-down phase from 365 to 290°C, the values for all moduli during both
anhydrous and hydrous pyrolysis remained approximately constant before increasing from
290°C to 25°C. The rapid increase observed in the shear modulus on the hydrous cool-down
phase may have been caused by the large fracture that developed on the 0° sample. The
vertical Poisson’s ratio shows that for hydrous pyrolysis, the values remained approximately
constant, while the values of Poisson’s ratio during anhydrous pyrolysis increased.

We observed that $\varepsilon$ nor $\gamma$ are never equal to or below zero, indicating that the com-
pressional and shear velocities traveling parallel to bedding (perpendicular to the symmetry
axis) always remained higher than the velocities traveling perpendicular to bedding (parallel to the symmetry axis), per equations 1 and 2. This was expected, as maximum velocity is defined by the fastest layers of the sample, while minimum velocities are defined by the slowest layers in the sample (Simm and Bacon, 2014). The larger increases in $\gamma$ during the hydrous cool-down phase were likely caused by fracture development and splitting of the layering parallel to bedding in the $0^\circ$ sample, resulting in much slower compressional and shear velocities traveling perpendicular to the bedding.

The hydrous pyrolysis on the ramp-up phase (Figure 19a) did not have enough time to significantly convert organic material to hydrocarbons and, therefore, there was little change in stiffness coefficients $C_{55}$ and $C_{66}$ as well as in the $\gamma$ Thomsen parameter. The cool-down phase (Figure 19b) showed a larger increase in stiffness coefficients and a decrease in $\gamma$ after cooling below 250°C compared to the ramp-up phase. Data from the cool-down phase of the hydrous pyrolysis in this study is similar to the responses in the stiffness coefficients and the gamma Thomsen parameter in previous works from Behura et al. (2009) (20a) and Elbaharia (2012) (20b). Data from Behura et al. (2009) were recorded under unconfined conditions and velocities obtained using a rheometer. Data from Elbaharia (2012) were recorded under a confining pressure of approximately 2000 psi, a heating rate of 6°C/hour, with velocities obtained from transducers operating at 1 MHz. Heating rates were slower in experiments from Behura et al. (2009) and Elbaharia (2012), which is likely why we did not see similar trends for $C_{55}$, $C_{66}$, and $\gamma$ on the ramp-up phase.

While the $\epsilon$ and $\gamma$ parameters showed promising results, the $\delta$ parameter was found to contain less reliable data on the hydrous cool-down phase. The $\delta$ parameter is the only Thomsen parameter dependent on the $C_{13}$ stiffness coefficient, where $C_{13}$ is given by equation 7. Note that $C_{13}$ is the only stiffness coefficient for a VTI medium that is dependent
on the compressional velocity in the 45° sample. We found that during the hydrous cool-
down phase, until the sample cooled to approximately 135°C, the calculation of the $C_{13}$ was
impossible due to negative values occurring beneath the square root in Equation 7:

$$
C_{13} = \sqrt{\frac{(4\rho V_{P45}^2 - C_{11} - C_{33} - 2C_{44})^2 - (C_{11} - C_{33})^2}{4} - C_{44}}. \quad (7)
$$

Upon further examination, the cause of the negative values underneath the square root
was caused by one or more of the following:

- Erroneously low $V_{P45}$ velocities
- Erroneously high $V_{S0}$ velocities
- Erroneously low $V_{P90}$ velocities

Due to the large fractures in the 0° sample, it is unlikely that the shear velocities were
too high. Likewise, due to the lack of fracturing in the 90° sample, it is unlikely the
compressional velocities were too low. Therefore, due to the large fractures occurring in
the 45° sample and sample deformation, it is likely that these velocities were too low to be
physically representative of the oil shale properties. To examine this further, we look at
physical constraints from Yan et al. (2013), which assert the following:

$$
\delta^- < \delta < \delta^+, \quad (8)
$$

where

$$
\delta^- = \varepsilon - 2r_0^2 \gamma(1 - r_0^2(1 + 2\gamma) + \sqrt{(1 - r_0^2(1 + 2\gamma))^2 + 2\varepsilon}) \quad \frac{1}{1 - r_0^2}, \quad (9)
$$
\[ \delta^+ = \frac{\varepsilon - 2r_o^2\gamma + r_o^2\sqrt{1 - 2r_o^2(1 + 2\gamma) + 2\varepsilon}}{1 - r_o^2}, \]  
\[ (10) \]

and

\[ r_o = \frac{\beta_o}{\alpha_o}. \]  
\[ (11) \]

For the hydrous pyrolysis cool-down phase especially, the data did not fall within the bounds of equation 8. This error affected the bulk modulus, shear modulus, and vertical Poissons ratio calculations on the hydrous cool-down phase as well. Several possibilities may have caused the anomalous velocities in the 45° sample, including:

- The pyrolysis causing deformation and fracturing in the sample
- The sample angle not being exactly 45°; Yan et al. (2013) found that angle errors as low as negative 2% can cause 20% of the data to lie below the lower boundary for a normalized \( C_{13} \)
- Sample heterogeneity

Despite the lack of reliable 45° velocities, the remaining data indicates that the increase in temperature caused kerogen to mature more efficiently after hydrous pyrolysis compared to anhydrous pyrolysis. During pyrolysis, several driving mechanisms affected whether the velocities increased or decreased. Velocities increased due to the transformation of organic matter, re-hardening of bitumen at high temperatures, and in the case of hydrous pyrolysis, brine vaporization combined with closure of pore space. Alternatively, velocities decreased due to increasing temperatures and fracture generation. The overpressure caused inside the kerogen lead to fractures and bitumen expulsion, which has also been observed by Lewan and Roy (2011). The bitumen expulsion and high temperature caused micron scale fracturing,
which significantly lowered the shear velocities in the rock. At lower temperatures, these fractures closed, resulting in a much higher shear modulus for the hydrous pyrolysis method. Overall, our findings have aligned with previous work, and have shown the importance of hydrous conditions in pyrolysis for optimum immature kerogen conversion.

CONCLUSIONS

We have presented temperature-dependent acoustic velocities measured during hydrous and anhydrous pyrolysis of oil shale from the Irati Formation. Our data show that both compressional and shear velocities decrease with increasing temperature. Our comparison between anhydrous and hydrous pyrolysis processes provide insight on the effects of brine and bitumen generation on seismic properties during pyrolysis. The presence of brine during pyrolysis resulted in a more effective hydrocarbon production process. Thus, at the same temperature, hydrous pyrolysis let to greater changes in seismic properties than anhydrous pyrolysis. Specifically, we find that:

- Shear velocities increased by up to 33% at the end of hydrous pyrolysis, while shear velocities only increased to a maximum of 3% at the end of anhydrous pyrolysis.

- Compressional velocities increased by up to 11% at the end of both hydrous and anhydrous pyrolysis.

- TOC decreased during hydrous pyrolysis by 5 wt%; negligible change in TOC was observed after anhydrous pyrolysis.

- Kerogen volume decreased by 11% after hydrous pyrolysis, while the kerogen volume increased by 2% after anhydrous pyrolysis.
• Hydrous pyrolysis had a greater effect on organic rich samples than anhydrous pyrolysis at the same temperatures

While anhydrous pyrolysis remains an effective means of producing from near-surface oil shale, our experiments have shown that higher temperatures are required (above 365°C) to produce hydrocarbons as effectively as hydrous pyrolysis. Our data should also be useful for building models for velocity and stiffness alterations during maturation (pyrolysis) of oil shale.

ACKNOWLEDGMENTS

We wish to thank Petrobras for providing oil shale samples and the DHI/Fluids and the OCLASSH consortia for funding to perform these experiments. We also would like to thank fellow colleagues in the Center for Rock Abuse and in OCLASSH, for their assistance, support, and input in the presentation of this work. Finally, we would like to thank Dr. Mike Batzle.
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properties, and textural characteristics of self resourcing reservoirs: GEOPHYSICS, 78, D223–D235.

LIST OF FIGURES

1. Core plugs at three different orientations, modified after Wang (2002) and Lo et al. (1986). We collected compressional waves from all three samples and shear waves from the 0° and 90° samples each time temperature increased. Using these waves and known lengths of the core samples before and after pyrolysis, we calculated compressional and shear wave velocities at each temperature step.

2. High-temperature, high-pressure equipment diagram. This diagram illustrates the ability for a sample to have a brine or nitrogen pore pressure. The black box shown controlled the temperature and temperature steps. P and S waveforms were collected manually using a pulser, switch box, and oscilloscope, and digitized with 10,000 points. Temperature data were observed and collected via the computer connected to the black box. Pressure data were observed using pressure transducers for pore and confining pressure. Diagrams of ISCO syringe pumps, computer, and oscilloscope were based on diagrams from Hasanov et al. (2015).

3. Temperature ramp-up and cool-down. This step graph (not drawn to scale) shows the temperature change during the entire pyrolysis process. Temperature began at 25°C, increased by 10°C every 10 minutes, and then held for 48 hours at 365°C. Each step in the graph represents a temperature step, and a datum point collected for waveform data. Data at 365°C were collected at least three times over the 48 hour period. The differential between confining and pore pressure was kept at approximately 800 psi.

4. Assembly of sample, transducers, and confining jacket. Picture made based off diagrams and pictures from Baharia et al. (2011). Flexible stainless steel confining jacket is a Swagelok CT series convoluted metal tubing, order number 321-16-X-1.

5. Compressional (5a) and Shear (5b) waveforms before and after pyrolysis. The solid
lines are the waveforms collected on the samples before pyrolysis at 25°C, and the dashed lines are the waveforms collected after pyrolysis at the same temperature. The actual compressional and shear travel times are determined by subtracting the transducer delay from the observed arrival time. Sample lengths were measured before and after pyrolysis to give an accurate velocity calculation.

6 Example pyrogram from aliquot of Irati oil shale samples as-is (no previously applied pyrolysis). All source rock analysis and total organic carbon determination performed by Weatherford Laboratories.

7 CT scans of 0°, 45°, and 90° samples; before pyrolysis (left column) and the same samples after hydrous pyrolysis (right column).

8 ESEM image before pyrolysis of the 90° sample. Large particles are quartz grains, darker areas kerogen, white areas are pyrite frambooids, and remaining layers are mostly illite and feldspars.

9 ESEM of one 45° sample after anhydrous pyrolysis (top) and the other 45° sample after (bottom) hydrous pyrolysis. The top image shows few changes as a result of anhydrous pyrolysis, but the bottom image shows bitumen generation on the surface.

10 FESEM of 90° sample before pyrolysis. Quartz, pyrite, clay and organic matter are clearly visible in the rock matrix.

11 FESEM of 90° sample after hydrous pyrolysis. The left image shows a much wider field of view of the sample, revealing the extent of the large fracture.

12 Oxygen Index vs. Hydrogen Index (12a) and Tmax vs. Hydrogen Index (12b). This data was collected using a programmed pyrolysis after implementing anhydrous and hydrous pyrolysis. Anhydrous sample indicates slight maturity increase with a decrease of HI and increase of Tmax. The hydrous sample shows higher maturity increase, as it
moves into the Type II kerogen window and closer into the mature oil generation window in (Figure 12b).

13 Compressional velocities. Two graphs in the left column represent compressional velocity data collected at each temperature step as temperature increased in the hydrous and anhydrous pyrolysis experiments for each of the core orientations. The two graphs on the right represent the data collected at each temperature step as temperature decreased, after being held at 365°C for 48 hours. Differential pressure was approximately 800 psi.

14 Shear Velocities. Two graphs in the left column represent shear velocity data collected at each temperature step as temperature increased in the hydrous and anhydrous pyrolysis experiments for each of the core orientations. The two graphs on the right represent the data collected at each temperature step as temperature decreased, after being held at 365°C for 48 hours. Differential pressure was approximately 800 psi.

15 Bulk modulus as a function of temperature. Triangles indicate ramp up, circles cool down. Bulk modulus values during hydrous pyrolysis remained consistently lower than bulk modulus values during anhydrous pyrolysis throughout the experiment. Differential pressure was approximately 800 psi.

16 Shear modulus as a function of temperature. Shear Modulus remained consistently lower throughout the temperature ramp up, and for most of the cool down, but as temperatures cooled and bitumen and hydrocarbons hardened, the shear modulus increased drastically, starting at approximately 250°C. Differential pressure was approximately 800 psi.

17 Poisson’s Ratio as a function of temperature. Differential pressure was approximately 800 psi.

18 Thomsen’s parameters as a function of temperature. Differential pressure was ap-
proximately 800 psi.

19 Ramp-up phase (19a) and the cool-down phase (19b) of stiffness coefficients $C_{55}$ and $C_{66}$ compared to $\gamma$ Thomsen parameter.

20 Re-digitized and plotted data of stiffness coefficients $C_{55}$ and $C_{66}$ compared to $\gamma$ from Behura et al. (2009) (20a) and Elbaharia (2012) (20b) as temperature increased. Note that under the VTI assumption, $C_{44}$ equals $C_{55}$.  

This paper presented here as accepted for publication in Geophysics prior to copyediting and composition.  
Table 1. Sample Dimension change from before to after pyrolysis

<table>
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<tr>
<th>Angle</th>
<th>Axial strain</th>
<th>Transverse strain</th>
</tr>
</thead>
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<td>0° Anhydrous</td>
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<td>0.009</td>
</tr>
<tr>
<td>45° Anhydrous</td>
<td>-0.049</td>
<td>0.017</td>
</tr>
<tr>
<td>90° Anhydrous</td>
<td>-0.031</td>
<td>0.003</td>
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<tr>
<td>0° Hydrous</td>
<td>-0.094</td>
<td>0.016</td>
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<tr>
<td>45° Hydrous</td>
<td>-0.070</td>
<td>0.025</td>
</tr>
<tr>
<td>90° Hydrous</td>
<td>-0.036</td>
<td>0.005</td>
</tr>
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Table 1. Source rock analysis of oil shale samples. TOC is the weight percent organic carbon in the sample. $S_1$ represents the volatile hydrocarbons released during first part of programmed pyrolysis. $S_2$ represents converted hydrocarbon compounds from the existing kerogen during programmed pyrolysis. $S_3$ is the oxygen containing compounds (namely CO$_2$) released during programmed pyrolysis. The $T_{max}$ is the temperature at maximum kerogen-to-bitumen-hydrocarbon conversion occurs ($S_2$ peak). $HI$ is the hydrogen index (100x$S_2$/TOC), and $OI$ the oxygen index (100x$S_3$/TOC). $S_2$/S$_3$ indicates the type of organic matter in the rock. Production index (PI) indicates the evolution level of the organic matter. $S_1$/TOC is the normalized oil content. Parameter descriptions after Ugohuoku (2010).

<table>
<thead>
<tr>
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<th>Before Pyrolysis</th>
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<th>After Hydrous</th>
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</thead>
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<td>25.90</td>
<td>20.70</td>
</tr>
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<td>$S_1$ (mgHC/g of rock)</td>
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<tr>
<td>$S_2$ (mgHC/g of rock)</td>
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<td>192.77</td>
<td>122.84</td>
</tr>
<tr>
<td>$S_3$ (mgCO$_2$/g of rock)</td>
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<td>0.29</td>
<td>0.13</td>
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<tr>
<td>$T_{max}$ (deg C)</td>
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<td>425</td>
<td>432</td>
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<td>$HI$ (mgHC/g of rock)</td>
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<td>&lt;1</td>
<td>&lt;1</td>
</tr>
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<td>&lt;1</td>
</tr>
<tr>
<td>$S_2$/S$_3$</td>
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<td>945</td>
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<tr>
<td>$S_1$/TOC*100</td>
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<tr>
<td>PI</td>
<td>0.05</td>
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Table 1. Mineralogy of Brazilian oil shale samples, weight percent of mineralogy only, and calculated volume percent of kerogen. “Trace” indicates less than 1 wt% of mineral present. Density values referenced (USGS, 1981; Worthington, 1990; Harvey et al., 2005; Mavko et al., 2009). Weight % values are normalized values assuming 100% mineral and clay content only. Using methods from Vernik (2016), we derive a volume % of kerogen.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>Before wt%</th>
<th>After Anhyd. wt%</th>
<th>After Hyd. wt%</th>
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<td>Calcite</td>
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<td>Trace</td>
<td>0</td>
<td>Trace</td>
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<tr>
<td>Dolomite</td>
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<td>1</td>
<td>Trace</td>
<td>1</td>
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<tr>
<td>Quartz</td>
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<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Potassium Feldspar</td>
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<td>10</td>
<td>10</td>
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<td>Plagioclase Feldspar</td>
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<td>Pyrite</td>
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<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Clays (Mica/Illite)</td>
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<td>42</td>
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<table>
<thead>
<tr>
<th><em>ρ</em> (g/cm$^3$)</th>
<th>Before vol%</th>
<th>After Anhyd. vol%</th>
<th>After Hyd. vol%</th>
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<tr>
<td>Kerogen</td>
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<td>51</td>
<td>53</td>
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Table 1. Comparison in velocities at 25°C before and after pyrolysis (in km/s). “P” and “S” stand for compressional and shear velocity, respectively. “A” and “H” stand for hydrous and anhydrous, respectively. 0, 45, and 90 denote the orientation of the bedding plane in the cored samples.

<table>
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<tr>
<th></th>
<th>P A0</th>
<th>P A45</th>
<th>P A90</th>
<th>S A0</th>
<th>S A90</th>
<th>P H0</th>
<th>P H45</th>
<th>P H90</th>
<th>S H0</th>
<th>S H90</th>
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<tbody>
<tr>
<td>ΔV (km/s)</td>
<td>+0.27</td>
<td>+0.10</td>
<td>+0.25</td>
<td>+0.03</td>
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<td>+0.15</td>
<td>+0.13</td>
<td>+0.28</td>
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<tr>
<td>ΔV%</td>
<td>+11%</td>
<td>+4%</td>
<td>+8%</td>
<td>+3%</td>
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<td>+6%</td>
<td>+4%</td>
<td>+27%</td>
<td>+33%</td>
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Table 1. Velocity Data Table. T is in °C, and velocities in km/s. “P” and “S” stand for compressional and shear velocity, respectively. “A” and “H” stand for hydrous and anhydrous, respectively. 0, 45, and 90 denote the orientation of the bedding plane in the cored samples. Additional error analysis is available in Gayer (2015).

<table>
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<tr>
<th>T (°C)</th>
<th>Vp</th>
<th>VpA45</th>
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<th>Vs</th>
<th>VsA90</th>
<th>VpH0</th>
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Figure 1: Core plugs at three different orientations, modified after Wang (2002) and Lo et al. (1986). We collected compressional waves from all three samples and shear waves from the 0° and 90° samples each time temperature increased. Using these waves and known lengths of the core samples before and after pyrolysis, we calculated compressional and shear wave velocities at each temperature step.

135x167mm (300 x 300 DPI)
Figure 2. High-temperature, high-pressure equipment diagram. This diagram illustrates the ability for a sample to have a brine or nitrogen pore pressure. The black box shown controlled the temperature and temperature steps. P and S waveforms were collected manually using a pulser, switch box, and oscilloscope, and digitized with 10,000 points. Temperature data were observed and collected via the computer connected to the black box. Pressure data were observed using pressure transducers for pore and confining pressure. Diagrams of ISCO syringe pumps, computer, and oscilloscope were based on diagrams from Hasanov et al. (2015).
Figure 3. Temperature ramp-up and cool-down. This step graph (not drawn to scale) shows the temperature change during the entire pyrolysis process. Temperature began at 25°C, increased by 10°C every 10 minutes, and then held for 48 hours at 365°C. Each step in the graph represents a temperature step, and a datum point collected for waveform data. Data at 365°C were collected at least three times over the 48 hour period. The differential between confining and pore pressure was kept at approximately 800 psi.
Figure 4. Assembly of sample, transducers, and confining jacket. Picture made based off diagrams and pictures from Baharia et al. (2011). Flexible stainless steel confining jacket is a Swagelok CT series convoluted metal tubing, order number 321-16-X-1.

82x61mm (300 x 300 DPI)
Figure 5a. Compressional (5a) and Shear (5b) waveforms before and after pyrolysis. The solid lines are the waveforms collected on the samples before pyrolysis at 25°C, and the dashed lines are the waveforms collected after pyrolysis at the same temperature. The actual compressional and shear travel times are determined by subtracting the transducer delay from the observed arrival time. Sample lengths were measured before and after pyrolysis to give an accurate velocity calculation.
Figure 5b. Compressional (5a) and Shear (5b) waveforms before and after pyrolysis. The solid lines are the waveforms collected on the samples before pyrolysis at 25°C, and the dashed lines are the waveforms collected after pyrolysis at the same temperature. The actual compressional and shear travel times are determined by subtracting the transducer delay from the observed arrival time. Sample lengths were measured before and after pyrolysis to give an accurate velocity calculation.
Figure 6. Example pyrogram from aliquot of Irati oil shale samples as-is (no previously applied pyrolysis). All source rock analysis and total organic carbon determination performed by Weatherford Laboratories.

65x39mm (300 x 300 DPI)
Figure 7. CT scans of 0°, 45°, and 90° samples; before pyrolysis (left column) and the same samples after hydrous pyrolysis (right column).

137x171mm (300 x 300 DPI)
Figure 8. ESEM image before pyrolysis of the 90° sample. Large particles are quartz grains, darker areas kerogen, white areas are pyrite framboids, and remaining layers are mostly illite and feldspars.

101x93mm (300 x 300 DPI)
Figure 9. ESEM of one 45° sample after anhydrous pyrolysis (top) and the other 45° sample after (bottom) hydrous pyrolysis. The top image shows few changes as a result of anhydrous pyrolysis, but the bottom image shows bitumen generation on the surface.

106x103mm (300 x 300 DPI)
Figure 10. FESEM of 90° sample before pyrolysis. Quartz, pyrite, clay and organic matter are clearly visible in the rock matrix.

88x70mm (300 x 300 DPI)
Figure 11. FESEM of 90° sample after hydrous pyrolysis. The left image shows a much wider field of view of the sample, revealing the extent of the large fracture.

54x26mm (300 x 300 DPI)
Figure 12a. Oxygen Index vs. Hydrogen Index (12a) and Tmax vs. Hydrogen Index (12b). This data was collected using a programmed pyrolysis after implementing anhydrous and hydrous pyrolysis. Anhydrous sample indicates slight maturity increase with a decrease of HI and increase of Tmax. The hydrous sample shows higher maturity increase, as it moves into the Type II kerogen window and closer into the mature oil generation window in (Figure 12b).
Figure 12b. Oxygen Index vs. Hydrogen Index (12a) and Tmax vs. Hydrogen Index (12b). This data was collected using a programmed pyrolysis after implementing anhydrous and hydrous pyrolysis. Anhydrous sample indicates slight maturity increase with a decrease of HI and increase of Tmax. The hydrous sample shows higher maturity increase, as it moves into the Type II kerogen window and closer into the mature oil generation window in (Figure 12b).
Figure 13. Compressional velocities. Two graphs in the left column represent compressional velocity data collected at each temperature step as temperature increased in the hydrous and anhydrous pyrolysis experiments for each of the core orientations. The two graphs on the right represent the data collected at each temperature step as temperature decreased, after being held at 365°C for 48 hours. Differential pressure was approximately 800 psi.

66x39mm (300 x 300 DPI)
Figure 14. Shear Velocities. Two graphs in the left column represent shear velocity data collected at each temperature step as temperature increased in the hydrous and anhydrous pyrolysis experiments for each of the core orientations. The two graphs on the right represent the data collected at each temperature step as temperature decreased, after being held at 365°C for 48 hours. Differential pressure was approximately 800 psi.
Figure 15. Bulk modulus as a function of temperature. Triangles indicate ramp up, circles cool down. Bulk modulus values during hydrous pyrolysis remained consistently lower than bulk modulus values during anhydrous pyrolysis throughout the experiment. Differential pressure was approximately 800 psi.
Figure 16. Shear modulus as a function of temperature. Shear Modulus remained consistently lower throughout the temperature ramp up, and for most of the cool down, but as temperatures cooled and bitumen and hydrocarbons hardened, the shear modulus increased drastically, starting at approximately 250°C. Differential pressure was approximately 800 psi.
Figure 17. Poisson's Ratio as a function of temperature. Differential pressure was approximately 800 psi.

66x40mm (300 x 300 DPI)
Figure 18. Thomsen's parameters as a function of temperature. Differential pressure was approximately 800 psi.

66x39mm (300 x 300 DPI)
Figure 19a. Ramp-up phase (19a) and the cool-down phase (19b) of stiffness coefficients C55 and C66 compared to γ Thomsen parameter.

66x40mm (300 x 300 DPI)
Figure 19b. Ramp-up phase (19a) and the cool-down phase (19b) of stiffness coefficients C55 and C66 compared to γ Thomsen parameter.

66x40mm (300 x 300 DPI)
Figure 20a. Re-digitized and plotted data of stiffness coefficients C55 and C66 compared to from Behura et al. (2009) (20a) and Elbaharia (2012) (20b) as temperature increased. Note that under the VTI assumption, C44 equals C55.
Figure 20b. Re-digitized and plotted data of stiffness coefficients C55 and C66 compared to from Behura et al. (2009) (20a) and Elbaharia (2012) (20b) as temperature increased. Note that under the VTI assumption, C44 equals C55.