Spectro-mechanical Characterization of Aromaticity and Maturity of Kerogens in Oil Shale at 6 nm Spatial Resolution

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Abstract:
In situ measurements of the chemical compositions and mechanical properties of kerogen help understand the formation, transformation, and utilization of organic matter in the oil shale at the nanoscale. However, the optical diffraction limit prevents attainment of nanoscale resolution using conventional spectroscopy and microscopy. Here, we utilize peak force infrared (PFIR) microscopy for multimodal characterization of kerogen in oil shale. The PFIR provides correlative infrared imaging, mechanical mapping, and broadband infrared spectroscopy capability with 6 nm spatial resolution. We observed nanoscale heterogeneity in the chemical composition, aromaticity, and maturity of the kerogens from oil shales from Eagle Ford shale play in Texas. The kerogen aromaticity positively correlates with the local mechanical moduli of the surrounding inorganic matrix, manifesting the Le Chatelier’s principle. In situ spectro-mechanical characterization of oil shale will yield valuable insight for geochemical and geomechanical modeling on the origin and transformation of kerogen in the oil shale.
Introduction

The extraction and utilization of organic matters (kerogen) in underground shale formations into usable petroleum and natural gas has recently become a rapid growing means of energy production in the world \(^1,2\). Organic matter is extracted by hydraulic fracturing (“fracking”), in which high-pressure liquid is pumped into the underground oil shale to mechanically fracture it, creating fissures that allow hydrocarbons to escape from nanopores in which kerogens reside. Kerogen is composed of both aliphatic and aromatic compounds (kerogen) and constitutes 1% to 15% of shale formations by weight. Fine-grained mineral particles such as quartz and clays \(^3,4\) form the inorganic matrix encapsulating this kerogen. The chemical transformation of immature kerogen into hydrocarbons depends on a variety of factors such as temperature, pressure, depth of the shale, and time \(^5-7\). These factors are generally well-understood and contribute to our estimations of recoverable oil shale reserves. However, the influence of local factors such as the size and mechanical properties of pores on kerogen formation and transformation is not well understood, as the nanopores are smaller than the spatial resolution of traditional spectroscopic techniques. Traditional infrared microscopy and Raman microscopy are bound by the optical diffraction limit to a half of the wavelength of light used, which is approximately several microns or several hundred nanometers, respectively \(^8\). Scanning electron microscopy (SEM), on the other hand, provides high spatial resolution over a large area, but it lacks chemical specificity for kerogens and requires vacuum conditions and high energy electrons that may alter or damage the sample \(^9,10\). Routine chemical analytical techniques such as gas or liquid chromatography, coupled with mass spectrometry, can reveal the identity of the kerogens, but these techniques are destructive and generally require macroscopic amounts of samples leading to loss of information regarding the spatial distribution of the kerogens in the shale \(^11,12\). None of these methods can determine
mechanical information, especially at the nanoscale, and that information is important for elucidating mechanical processes on kerogen generation and transformation.

Recently, two atomic force microscopy (AFM) based infrared microscopy methods have been applied to the study of oil shale. Photothermal induced resonance (PTIR, also commercially known as AFM-IR) spectroscopy has been coupled with traditional petrographic methods to characterize the microscale heterogeneity of organic matter. However, the AFM-IR technique provides only ~100 nm spatial resolution on oil shales, insufficient to image the nanopores and kerogen in oil shales. Also, the AFM contact mode that the PTIR operates in is vulnerable to tip wear when scanning over rigid and rough surface of shale. Scattering-type scanning near-field optical microscopy (s-SNOM), coupled with a synchrotron light source, reveals the chemical heterogeneity at an improved spatial resolution of ~20 nm. However, s-SNOM operates in the AFM tapping mode, which is unable to provide quantitative mechanical information. Besides, organic matters produce only weak signals in s-SNOM measurements, compared with those using the photothermal-based PTIR technique.

Here, we utilize peak force infrared (PFIR) microscopy to address the need for multimodal nondestructive characterizations of kerogen in oil shale with high spatial resolution, chemical sensitivity, and the ability to yield mechanical information. PFIR microscopy is an AFM-based infrared microscopy recently developed by our research group that simultaneously provides infrared imaging and mechanical mapping, in addition to broad-band spectroscopy, all at <10 nm spatial resolution. The scheme of the home-built PFIR microscopy apparatus is depicted in Figure 1 and described in the Method section. The local photothermal expansion of infrared absorption is transduced by the mechanical response of the AFM cantilever, revealing the chemical heterogeneity of kerogen. The peak force tapping mode of AFM, in which PFIR microscopy is
operated, measures the moduli of the sample surface. The correlative infrared and mechanical responses enable us to decipher correlations between kerogen composition and local matrix properties. The characteristic infrared absorption of aliphatic and aromatic hydrocarbon reveals the nanoscale aromaticity, and enables further deduction of the in situ maturity of the kerogen in the oil shale.

Figure 1. PFIR experimental scheme and data collection. (a) Experimental setup of the PFIR apparatus used for infrared and mechanical characterization of kerogen in shale. (b) The cantilever deflection curve measured with laser-induced contact resonance (red curve) and subsequently without the laser-induced contact resonance. (blue curve) (c) The laser-induced mechanical response of the cantilever after background subtraction. Contact resonance and baseline offset (Δ) are excited due to rapid thermal expansion of the sample from absorption of the pulsed infrared laser. The value of baseline offset or the integration of contact resonance bands are used as the PFIR signal. (d) Subsequent fast-Fourier transform produces the PFIR trace, in which a low frequency peak is integrated to obtain the chemical signal.
Results

The immature oil shale samples used in this study were obtained from outcrops in the Eagle Ford shale play in southern Texas. The outcrop samples were pulverized into fine powders (10 to 25 μm, determined by an optical microscope) and mechanically pressed under 6000 psi into flat pellets for the PFIR measurements. PFIR images were measured on 3 μm × 3 μm sample surface. PFIR images were completed in the PFT mode at a scan rate of 0.2 Hz, a peak force set point of 9 nN, a PFT frequency of 4 kHz, and a sample oscillation amplitude between 50 to 90 nm, depending on surface roughness. PFIR images were obtained in approximately 40 minutes each. Signal was collected in real time with a data acquisition card (PXI-5122, National Instrument) at 50 M samples/second sampling rate. The complementary topography, adhesion, and modulus maps were collected at a PFT frequency of 2 kHz. These measurements were obtained separately from the PFIR measurements to avoid any possible signal cross talk between photothermal expansion and AFM probe indentation.

PFIR microscopy reveals the distribution of infrared responses from kerogen in immature oil shale together with correlative mechanical properties of modulus and adhesion. The PFIR measurements are displayed in Figure 2. The topography of the sample (shown in Fig. 2a) reveals the surface roughness. Adhesion (Fig. 2b) and modulus (Fig. 2c) images provide the mechanical properties of the same region. The topography and mechanical images do not provide indications to chemical compositions. The distribution of aliphatic hydrocarbons (shown in Fig. 2d) is revealed by the PFIR microscopy at the infrared frequency of 2920 cm⁻¹ that is characteristic of alkyl CH₂ asymmetric stretch. Similarly, the distribution of the aromatic hydrocarbons (displayed in Fig. 2e-f) is revealed at the infrared frequency of 3032 cm⁻¹, which is
resonant with the aromatic CH stretch. Spectroscopic contrasts within each image indicate that different types of kerogen are spatially localized within the sample at the nanoscale. The infrared frequencies of 2920 cm\(^{-1}\) and 3032 cm\(^{-1}\) are chosen as they can be differentiated within the accompanying spectra and do not overlap with other infrared-active species found within oil shale. These two frequency responses allow us to affirm the identities of kerogen as containing either aromatic hydrocarbons, aliphatic hydrocarbons, or both if signal overlap is present in images or spectra.

Individual point spectra (Fig. 2g) are taken to further elucidate the identity of the kerogen. The collection of PFIR spectra was achieved by sweeping the frequency of the OPO while the AFM probe remained fixed at a location of interest while under PFT mode feedback. The PFIR signal from the contact resonance normalized by the laser power was plotted versus the infrared frequency to form the PFIR spectrum. Distinct chemical identities are revealed throughout the sample surface, as suggested by the differences from point spectra. The spectrum originating from the 2920 cm\(^{-1}\) active area (gray spectrum) further supports the notion that PFIR signal in Fig. 2d originates from aliphatic hydrocarbon rich kerogen due to the pronounced peak at 2920 cm\(^{-1}\). Conversely, the spectra taken at the 3032 cm\(^{-1}\) areas in Fig. 2e (red, blue, and green spectra) show the presence of aromatic rich constituents within the shale. In these studies, the PFIR signal at 3032 cm\(^{-1}\) is much weaker than the signal at 2920 cm\(^{-1}\). This can be attributed to a relatively low aromaticity, or concentration of aromatic hydrocarbons.

A spatial resolution of 6 nm is extracted from the cross-section marked in Fig. 2f as the width between 10\% and 90\% of the edge height of the PFIR signal. The apex radius of the probe used in this measurement is found to be 30 nm by identifying spatial frequencies from a scan on rough titanium calibration sample, following the standard tip-quantification procedure of the Bruker
AFM. The spatial resolution of PFIR surpasses the tip radius, because the tip-sample contact area in the peak force tapping mode is smaller than the full probe radius due to small indentations in each tip-sample contact.

![AFM and PFIR images](image)

Figure 2. PFIR acquired images and point spectra of an immature 3 μm × 3 μm Eagle Ford shale sample. (a) Topography of the shale. The scale bar is 1 μm. (b) Adhesion between AFM tip and the sample. (c) Modulus map of the shale sample surface. (d) PFIR image taken at 2920 cm⁻¹, indicating the presence of aliphatic hydrocarbon compounds. (e) PFIR image taken at 3032 cm⁻¹, characteristic of aromatic compounds. (f) A 330 × 330 nm PFIR image taken at 3032 cm⁻¹ positioned within the location of the white box in 2e. (g) Point spectra taken from chosen areas on the surface as indicated by the colored arrows in the accompanying PFIR images. (h) A spatial resolution of 6 nm is observed from a cross-section in (f), indicated by the yellow line.
The multimodal capability of PFIR microscopy allows establishing correlations between chemical signal and its accompanying mechanical signal. **Figure 3** displays another multimodal PFIR measurement of the same oil shale sample at a different $3 \mu m \times 3 \mu m$ area, in which more aromatic compositions are revealed than in the region of Figure 2. **Fig. 3a** shows the topography of the region. The PFIR images from the aliphatic (**Fig. 3c**), aromatic hydrocarbons (**Fig. 3d**), and accompanying modulus map (**Fig. 3b**) are processed to obtain the correlations between chemical compositions of kerogen packets and moduli of surrounding inorganic matrix. The spectral intensity at individual locations are correlated with the average moduli of their surroundings. **Fig. 3e** shows the average moduli of the surrounding of both aliphatic hydrocarbon and aromatic hydrocarbon versus the distance from the hydrocarbons. The detailed procedure of the data processing is included in the Supplementary Figure S1. The correlation between the surrounding moduli and the distance reveals that kerogen of aliphatic hydrocarbon correlates with low-modulus surroundings; in contrast, kerogen of aromatic hydrocarbons correlates with high-modulus surroundings.

How should we understand such correlations? The organic matter precursors of the kerogen from the $3 \mu m \times 3 \mu m$ region should have the same initial maceral composition (organic matters from ancient organisms), because of the small size of the region. Under external pressure, the high-modulus inorganic surroundings transfer higher pressure to the organic matters trapped within the matrix than low-modulus surroundings, leading to different local pressure levels on the initial maceral compositions. Also, aromatic kerogens are known to have higher density than aliphatic kerogens $^{16}$. As organic matter matures, kerogens of aliphatic hydrocarbons are gradually transformed into kerogens of aromatic compositions through a series of chemical reactions $^{17}$. According to Le Chatelier's principle, higher external pressure favors chemical species with
smaller volume (or higher density) in chemical reactions. Therefore, the high-modulus matrix favors the generation of high density kerogens that contain more aromatic composition. Le Chatelier’s principle explains the observed correlations between the chemical identify and moduli of the surrounding inorganic matrix. Note that we do not rule out other factors in the chemical transformation of the kerogen. However, since the area of study (3 μm × 3 μm) is very small, macroscopic parameters such as original composition of the kerogen, depth of the sample buried, and temperatures experienced during the past millions of years are practically the same. Therefore, the modulus of inorganic matrix is an influencing factor of the transformation of the kerogen identity.
**Figure 3. Chemical and mechanical correlation as observed with PFIR.** (a) Topography obtained from a 3 μm × 3 μm area of an Eagle Ford shale outcrop sample. The scale bar is 800 nm. (b) Modulus obtained over the same area. (b) PFIR image at 2920 cm⁻¹ showing the presence of aliphatic hydrocarbon groups. (d) PFIR image at 3032 cm⁻¹ showing the presence of aromatic hydrocarbon groups. (e) Correlation between chemical identities and surrounding modulus values. Data from the aromatic-modulus correlation are depicted in red and data from the aliphatic-modulus correlation are depicted in blue. The average modulus (4.5 GPa) is obtained by averaging the modulus over the entire image in (b).

We can also derive the aromaticity of the region of measurement. Aromaticity, the relative amount of carbon atoms in a sample that exist in aromatic rings, is an important factor for utilization of the kerogen as it is a factor to the overall quality of an oil shale. Aromaticity is also important when assessing the potential risks that fracking poses to surrounding water basins and water sheds due to the carcinogenic nature of many organic aromatic compounds. The extracted numerical data from the chemical maps in Fig. 3c-d were normalized and plotted as a point-density map. Aromaticity was found with a method similar to that used by Craddock et al. The intensity of each data point belonging to the 3032 cm⁻¹ set was summed and divided by the sum of each data point belonging to 3032 cm⁻¹ and 2920 cm⁻¹. Data points less than 20% of maximum signal magnitude after normalization were attributed to the inorganic matrix and not used in determining aromaticity. **Figure 4** displays a heatmap from correlating normalized intensities of aliphatic (2920 cm⁻¹) and aromatic hydrocarbons (3032 cm⁻¹) from PFIR images. The aromaticity was extracted similarly to a method previously employed by Craddock et. al. We obtain the aromaticity directly by summing the relative intensity of each data point from 3032 cm⁻¹ and dividing it by the total sum of all organic data point intensities (2920 cm⁻¹ and 3032 cm⁻¹). This method establishes an aromaticity of 0.13, typical to values reported previously of shales of the same origin.
Figure 4. Aromaticity measurement obtained through PFIR. A heatmap of normalized PFIR signal intensities produced by plotting each individual pixel corresponding to PFIR intensity at 2920 cm\(^{-1}\) with the PFIR intensity at 3032 cm\(^{-1}\). PFIR intensities accounting for the weakest 20% of maximum signal are attributed to the inorganic matrix within the sample and is ignored for aromaticity calculation. The data is extracted from measurement shown in Figure 3.

The ratio between aliphatic hydrocarbon and aromatic hydrocarbon infrared responses allows us to derive the in situ maturity of the kerogen. The maturity of kerogen is an indicator of a reserves shale-oil production quality\(^{17,24}\). In FTIR characterization of oil shale, peak-ratios from infrared spectra correlate with the thermal maturity and classification of the kerogen within oil shale samples\(^{17,23,25}\). As previous literature\(^{13}\) and our measurements above have revealed, the chemical composition of kerogen varies greatly across sub-micron length scales. The maturity and
classification of kerogen at spatial scale below the optical diffraction limit is inaccessible \(^{17,22,26}\) by traditional infrared spectroscopy. In contrast, the high spatial resolution of the PFIR microscopy and its ability to collect spectra at individual location enables evaluation of maturity at the nanoscale. In our study, we collect PFIR spectra from eight locations on the sample of Figure 3 and four locations from Figure 2. The location of the measurement is marked in Supplementary Figure S2. PFIR spectra allow for the C-factor (the oxygenated character) and A-factor (the saturated character) to be obtained from normalized spectra by creation of a van-Krevelen diagram.

The maturity of the kerogens was completed in a method according to that used by Ganz et al.\(^ {23}\) To obtain the relative aliphatic hydrocarbon content, the A-factor was calculated as \([I_{2920}]/[I_{2920} + I_{3032}]\) To obtain the relative oxygen content in each sampled area, the C-factor was calculated as \([I_{3645}]/[I_{2920} + I_{3032}]\). The sharp peak at around 3645 cm\(^{-1}\) was chosen for this calculation as it is indicative of the O-H stretching vibration. 2920 cm\(^{-1}\) and 3032 cm\(^{-1}\) result from aliphatic (CH2 asymmetric stretch) and aromatic (CH stretch) hydrocarbons groups, respectively. This method slightly differs from Ganz’s method since 3645 cm\(^{-1}\) was chosen as the oxygenated band instead of 1710 cm\(^{-1}\) to ensure the laser spot size and focus of our OPO remains unchanged throughout the measurement. Figure 5 shows the resulting van-Krevelen diagram of kerogen maturity obtained through analyzing peak ratios obtained at different locations along the sampled areas. In our study, the A-factors and C-factors are calculated through a method similar to other commonly employed methods \(^ {13,22,23}\). The method of treatment is described in the Materials and Methods section. The measurements reveal varying kerogen maturity from adjacent organic pockets. Eagle Ford shale play is classified as type II kerogen, since the maceral composition came primarily from plankton \(^ {27}\). Our measurement provides the ability to estimate the level of the maturity and reveals heterogeneity of the maturity from the nanoscale.
Figure 5. Van-Krevelen diagram obtained from point PFIR spectra. Twelve spectra of organic pockets within the Eagle Ford shale outcrop sample are used to generate this plot. The colors indicate two separate 3 μm × 3μm measurement regions, indicated in Supplementary Figure S2. For each data point, the relative intensities of saturated functional groups (A-factor) is plotted against the relative intensities of oxygenated functional groups (C-factor) within a single point spectrum.

Discussion
PFIR microscopy is advantageous for investigation of oil shale, compared with the existing AFM-based infrared techniques. The 6 nm spatial resolution from PFIR on oil shale is far greater than the ~50 nm spatial resolution of the AFM-IR technique \(^ {13,28}\) and the ~20 nm spatial resolution of s-SNOM \(^ {14}\). The peak force tapping operational mode of PFIR is suitable for shale surfaces, which are typically rough and sticky. In comparison, the contact mode AFM that the AFM-IR technique operates in cannot handle rough and sticky surface due to tip wear and sample scratches. The quantitative mechanical information from the peak force tapping in PFIR microscopy enables correlations between the mechanical and chemical responses in one operational mode. In contrast, the tapping mode s-SNOM does not provide any access to the quantitative mechanical information
of the sample. The chemical sensitivity of PFIR microscopy is advantageous over scanning electron microscopy or atomic force microscopy that only provides the morphology of the sample. In addition, PFIR microscopy is nondestructive to the sample and operates under ambient conditions, which is advantageous over the scanning electron microscopy that requires high-energy electrons and high-vacuum conditions. PFIR microscopy is suitable for providing both chemical and mechanical information for samples of oil shale.

Our investigation on oil shale demonstrates the presence of nanoscale heterogeneity of the chemical compositions of kerogen and associated aromaticity and maturity. The correlation between the mechanical and chemical compositions revealed by our method suggests that the local mechanical modulus of the inorganic matrix influences the chemical transformation of the kerogens. Higher modulus inorganic matrices favor the generation of kerogen with high aromatic compositions over lower modulus inorganic matrix. This correlation can be extremely valuable toward strategies in hydraulic fracturing, given the environmental risk that is associated with the release of the aromatic kerogen during this process. If the aromatic composition resides in nanopores with higher moduli, the pressure of the hydraulic fracturing can be precisely controlled to minimize the release of aromatic hydrocarbon kerogen, while allowing the aliphatic hydrocarbons to be extracted.

**Conclusion**

In summary, we have demonstrated that PFIR is a non-destructive nanoscale-resolution multimodal infrared and mechanical characterization technique with great potential for use in the study of kerogen in oil shales. Using this method, nanoscale heterogeneity of chemical compositions, aromaticity, and maturity have been revealed and the aromaticity of the kerogen has been found to correlate with the local mechanical properties of the inorganic matrix. We hope that
this high spatial resolution imaging/analytical methodology will constitute an important step affording more sophisticated geochemical modeling aimed at understanding the origin and transformation of kerogen in geological settings.

**Methods**

The scheme of the home-built peak force infrared microscopy apparatus is depicted in **Figure 1**. The details of the optical setup are described in our recent literature 15. An atomic force microscope (Multimode AFM with Nanoscope V, Bruker) is operated in the peak force tapping (PFT) mode 29. In PFT mode, the AFM cantilever is held stationary and the sample surface is oscillating vertically at a low frequency (typically 4 kHz) by a piezo stage. (**Fig. 1a**) Near the upper turning point of the sample oscillation, the AFM tip momentarily contacts the surface of the sample, and the AFM cantilever is pushed upward, leading to vertical deflections. The maximal vertical deflection of the cantilever is used as the set point in the PFT feedback mechanism. After momentary contact, the sample surface is lowered by a piezo stage to finish one PFT cycle. PFT feedback maintains a controlled tip indentation on the sample surface for each PFT cycle to avoid tip wear. Infrared laser pulses of 25 ns duration from a frequency tunable optical parametric oscillator (OPO, NT377, EKSPLA) are synchronized with the PFT cycles at a half of the PFT frequency. Photothermal expansion of the sample is generated by the laser at every other peak force tapping cycle and transduced by the cantilever deflection of the AFM. (**Fig. 1b**) Cantilever responses from the PFT cycle without laser excitation is recorded as a reference for background subtraction. (**Fig. 1c**) The contact resonance oscillations are observed and their amplitudes are extracted through Fourier transform to obtain the PFIR signal. (**Fig. 1d**) The PFIR image is formed by collections of the PFIR signal at a fixed laser frequency as the AFM tip is scanned over the shale sample. The PFIR spectrum is collected by scanning the frequency of the light source when
the AFM tip is placed at a location of interest. The complementary images of modulus and adhesion are derived from the Derjaguin–Muller–Toporov contact mechanical model \(^{30}\) from the cantilever deflection during the tip-sample contact.

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**Author contributions**

X.G.X and D.S.J. conceived the original idea. L.W., H. W. and X.G.X. built the prototype of the instrument. D.S.J. collected the experimental data. D.S.J., X.G.X participated in the data analysis. X.G.X. and D.S.J. wrote the manuscript. L.W. and H.W. helped edit the manuscript.

**Competing interests**

The Authors declare no Competing Financial or Non-Financial Interests.

**References**


