Rediscover Your Reservoir with Reservoir RockHound

Introduction

In today's competitive market, knowing the composition of the fluids in your well and determining from which zone(s) each is coming can save money and time. Is it hypersaline brine mixed with CO2 and light hydrocarbon gases? Which gases are present? Where and how much of each fluid is coming from each zone penetrated? Further, knowing the precise mineralogy (minerals present and in what quantities), total organic carbon (TOC), thermal maturity, silica/clay ratio to ascertain brittleness, microfossil identification and distribution, and porosity and how they change throughout the reservoir, could be very important. Combined, these are useful data for better determining where to land a lateral and exactly where and how best to stimulate the well.

The interaction between the chemical composition of the fluids and solids used in completing or stimulating a well and those that exist in the subsurface affects the physics and chemistry of your successful well. If you know confidently which fluids are in your well and from where they come, and add a solid knowledge of the heterogeneity of the petrology, mineralogy and cement(s) throughout your reservoir, you can better determine the most efficient way to stimulate your reservoir, or choose the best methods to use in secondary recovery.

WellDog has practical and fit-for-purpose technology that can help one achieve optimal wells. The fluids downhole can be determined using WellDog's Downhole Reservoir Raman Spectroscopy (DRRS) wireline tool, and the composition of the reservoir rock and fluids (free and adsorbed) can be evaluated using WellDog's Raman Spectroscopy laboratory services. Derived results can enable drilling fewer wells that are optimally completed to suit the reservoir, thus leading to potentially higher recovery factor.

Raman Spectroscopy – A Brief Introduction

Raman Spectroscopy is an old technology to which WellDog has added new practical applications. It is named after Sir C.V. Raman, one of the scientists that discovered it in the 1920s, earning him the Physics Nobel Prize in 1930. In the classical description, photons of light inelastically scatter off molecules, resulting in the transfer of a small amount of energy. When energy is transferred to the molecule (termed Stokes Raman scattering), the molecule begins to vibrate, and the scattered photon is shifted in color. The magnitude of the Raman shift is characteristic of the molecular vibration. In modern times, a monochromatic laser is used as the excitation source and specialized filters along with sensitive photon detectors are used to capture Raman scattering for chemical fingerprinting of materials. The colors of the scattered photons are different for each molecule and are based on the chemical bonds within the molecules.

Raman spectra are acquired using a petrographic microscope to focus a laser onto the surface of the sample, on an area about one square micron. The light scattering from the sample passes through a filter and a Raman spectrum from the material in that area is recorded on a CCD-detector (Inset to Figure 1).

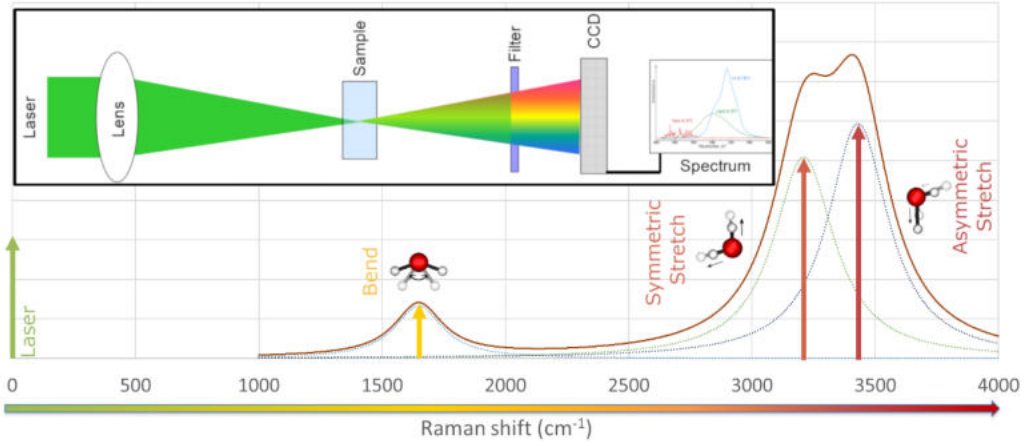

Figure 1. Example Raman spectrum showing three Raman-active molecular vibrations of water: bending, symmetric stretching, and asymmetric stretching. Inset. Schematic of the process of collecting Raman spectra.

Because each different molecule has a distinct set of vibrations and frequencies (Figure 1), different minerals and polymorphs can be accurately determined by the resulting Raman. These spectra can be used to identify and quantify a variety of materials on a molecular vibrational basis including thousands of minerals (see Figure 2), organic material in source rocks (Figure 3), as well as gases (Figure 4). Because it's based on molecules and the arrangement of the molecular bonds, one can even tell the difference between minerals which have the same elemental composition but different shapes (see right-Figure 2). The polymorphs of titanium oxides and iron sulfides are easily distinguished in Raman spectra because the atoms in those crystals are arranged differently, and therefore the vibrations are different.

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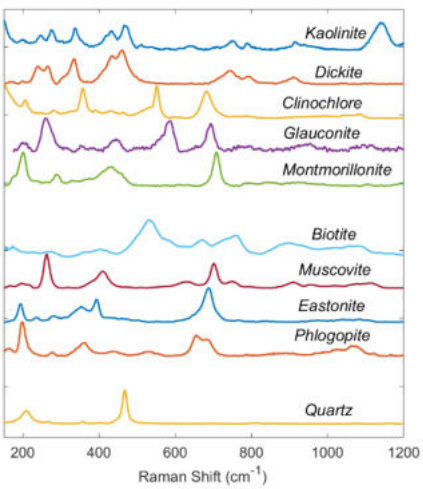


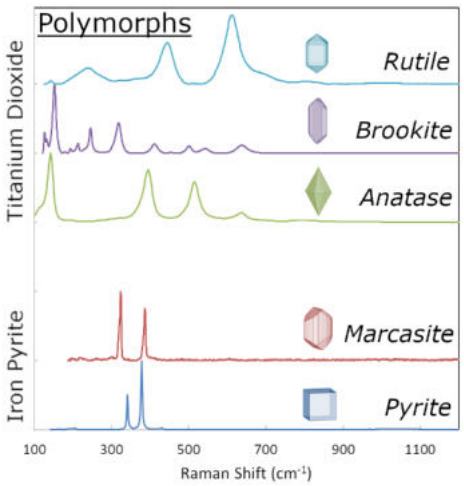
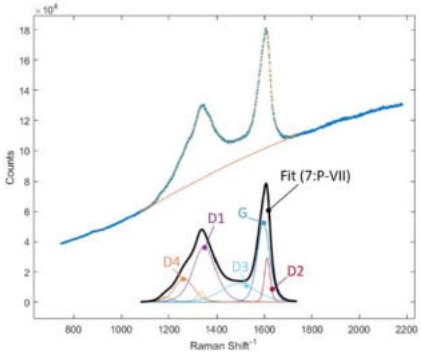


Figure 2. Example spectra of some common clays, micas, and Quartz. Because this technique is based on molecular vibrations, thousands and thousands of minerals, even polymorphs, can be differentiated, even if they have identical elemental compositions, due to different molecular arrangements in the crystalline structure.

Carbon in source rock samples can also be differentiated. Figure 3 shows a typical spectrum for carbon. There are two bands, commonly known as D (disorder) and G (graphite). In reality, there is much more that can be understood here. First, note the luminescence background, which is the sloping orange baseline underlying the actual Raman signal. Most Raman spectra collected from materials exhibit this behavior, which is often corrected for by subtracting a polynomial fit to flatten out the spectrum. Second, as shown below, the D band is a combination of many bands, some of which overlap with the G-band. Even the G-band is composed of overlapping peaks. These complexities in the spectra allow for differentiation of carbon types as well as a characterization of thermal maturity as will be discussed later.



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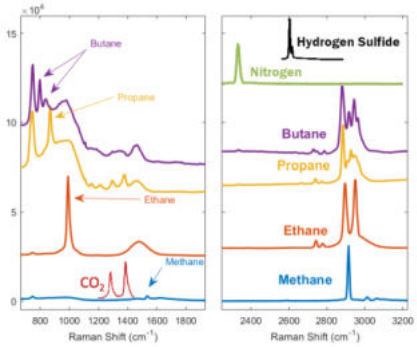

B

Figure 3. A. Typical Raman spectrum of organic material from source rock showing baseline correction and peak fitting to reveal underlying structure useful for carbon typing and maturity assessment. B. Raman spectra for several gases important in the oil and gas industry.

In Figure 3B, Raman spectra are shown from a variety of gases important in the oil and gas industry, including small hydrocarbons, carbon dioxide, nitrogen and hydrogen sulfide. These can be measured *in situ* down the wellbore dissolved in formation fluids, at the surface through a pressure manifold and even mid-stream in the pipeline. From Reservoir RockHound to SweetSpotter and beyond, WellDog Raman spectroscopy technologies can be applied to a wide range of well prospecting, development and production scenarios.

WellDog Raman Spectroscopy Solutions

How can Raman spectroscopy technology be utilized to better understand the reservoir? To fully understand the reservoir, one needs to know the composition of the organic and inorganic grains in the rock, the mineralogy of the rock and associated cement, porosity, permeability, the composition of the fluids, and how and where all these pieces come together to create the best reservoir sweet spots.

WellDog has a two-part solution to answer these challenges. Part one is a Downhole Reservoir Raman system to quickly understand the fluids in the wellbore. Part two is a laboratory Raman microscope system that yields information about the solids and pore spaces of the reservoir. It is a nondestructive, repeatable, objective way to look at cuttings, core, plugs, or thin sections.

First, which fluids are present? Water? Hypersaline brine? CO2? Nitrogen? Light hydrocarbons? Wet Gas? Dry gas? Condensate? It is important to know and understand what the fluids are and where they reside and migrate from.

SweetSpotter – Downhole Reservoir Raman System (DRRS) – Know Your Fluids

SweetSpotter is the first commercial reservoir evaluation analysis technology specific to unconventional oil and gas. The technology was originally developed to find sweet spots in coal bed methane developments, and since 2014 WellDog has been developing

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shale-based applications for the technology. SweetSpotter was developed with the target of doubling the number of producing fractures. This is accomplished by using the industry's only wireline deployed downhole Raman spectrometer to directly identify locations of producible hydrocarbons across formations. Successful field trials were completed with WellDog's industry partner in the Marcellus Shale. This next-generation downhole technical service uses lasers and sophisticated advanced state-of-the-art detectors to identify the locations where hydrocarbons occur in shale formations, allowing producers to focus development efforts, reduce drilling costs, optimize production and potentially reduce the number of hydraulic fracturing stages and associated water usage.

The Downhole Reservoir Raman System (DRRS) is a wireline conveyed Raman spectrometer and physical sensor platform illustrated in Figure 4. It is a robust tool that can measure low ppm levels of hydrocarbons dissolved in water in a well, while discriminating in real time between the presence of dissolved methane, free methane gas and other light hydrocarbons. [from URTEC #2431773]

Figure 4. SweetSpotter 3" downhole tool and truck in the field. Lower picture shows a new downhole tool being built in the lab.

DRRS data provide a real time estimate of plume formation in the well following perforation, allowing for an estimate of the mass of methane entering the well per unit time. This flux measurement provides an estimate of the composition and relative richness of different stratigraphic intervals within a reservoir. The results of a field trial with an industry partner in the Marcellus Shale showed that the most productive interval was the Upper zone, producing gas to the well bore at a considerably faster rate than the more TOC rich and higher porosity Basal zone. These results challenge an established paradigm of unconventional resource evaluation which is focused mostly on high Uranium and TOC intervals for completion of laterals. Based on measured plume concentrations in the two field trials, the estimated resource density (i.e. the mass of methane per volume of rock) is highest in the Upper Marcellus. Therefore, it makes sense to prioritize completion of the upper zone with a lateral, rather than the middle or basal units. [from URTEC #2431773]

Data from the DRRS tool can be mapped (Figure 5) and used to create a better drilling, lateral kick-off point, completion and hydraulic fracturing program, specifically targeting the zone(s) with the highest concentrations of the desired product and thus enhancing long term production while reducing overall asset development cost.

Figure 6 demonstrates the high vertical resolution offered by the DRRS in locating where methane enters the wellbore, thereby helping to locate the most productive zones in a vertical well and optimize the placement of laterals. The results of this test suggest that the optimal landing zone for a lateral in this well might target the Upper zone with a single completion since this zone delivered the highest flux of methane to the well bore, i.e., the highest mass of methane per unit of time, which we refer to as the Producibility Index (PI).

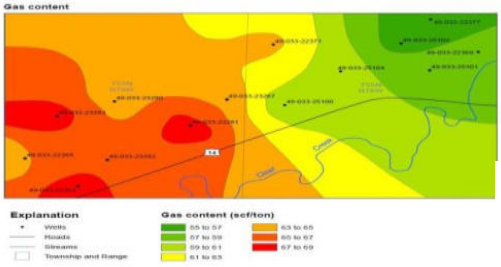

Figure 5. Mapped gas concentrations.

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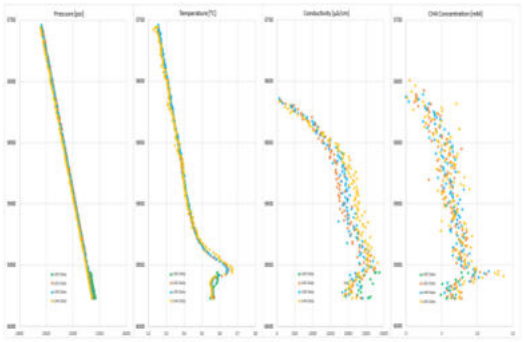

Figure 6. Pressure, temperature and conductivity readings during DRRS logging of the Upper zone. Note how the conductivity increases with time as a result of counter current flow of ions into the well bore as a result of coupled osmosis-diffusion processes. Last panel shows the time integrated methane concentration i.e., flux, measured with the DRRS (mM units).

Having addressed the downhole fluids and where they come from, understanding the rock from which they come could add a crucial bit of information to improve drilling and completion decisions. Enter Reservoir RockHound. One challenge

Issues with vitrinite reflectance (Ro) and pyrolysis

The current standard to determine thermal maturity is vitrinite reflectance (Ro). Although standards exist, there are issues with consistency. Results can vary depending on how an individual interpreter feels that day – tired, happy, distracted… - and who trained them, to name just a couple of variables. Finding vitrinite in a sample is also not a given, as many source rocks do not come from woody plants.

There are many challenges in determining thermal maturity for the purposes of source rock assessment. Important factors are temperature, time, and pressure, where temperature is the most sensitive parameter in hydrocarbon generation. Thus, reconstruction of temperature history is essential when evaluating petroleum prospects. Tissot said, “No measurable parameter can be directly converted to paleotemperature. Maturation indices such as vitrinite reflectance, T_{max}, (and others) … offer an indirect approach. All these are a function of the thermal history through rather complex kinetics, frequently influenced by the type of organic matter.” [Reference]

Vitrinite is a powerful method favored by petrographers for coal, where that woody maceral is commonplace. In shales, however, and marine shales in particular, vitrinite can be extremely rare, and if old enough, practically non-existent. It’s a tedious measurement – anisotropy affects this structured woody material, which polishes up differently based on which face is oriented upwards. That means that the petrographer needs to locate and perform measurements on at least 50 bits of vitrinite, ideally a hundred, and be careful to avoid recycled material, or solid bitumen, which can polish to a similar luster, but has a different correlation to thermal maturity.

How hard is this process? Figure 7 gives some sense of the difficulties associated with Ro calculation. A study was done in which the same set of samples were sent to 22 laboratories for characterization using the ASTM standard method for vitrinite reflectance. Figure 7 shows some of the better results which are still plagued with enormous variability in the answers. The study suggested that these issues are related to operator training and background. In other words, one needs to have a lot of confidence in one’s petrographer and trust their consistency in analysis from one sample to the next.

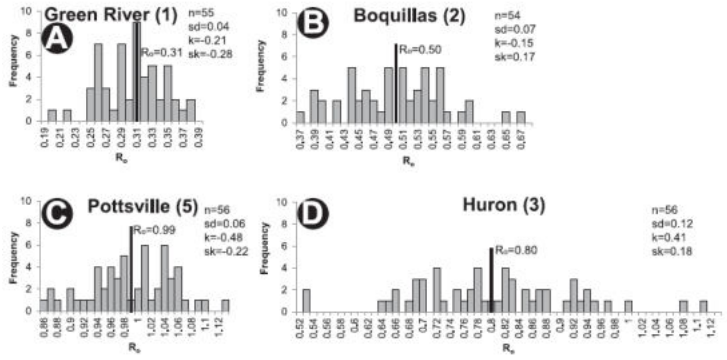

Figure 7. Examples from a vitrinite reflectance study showing how varied results can be from interpreter to interpreter.

Raman spectroscopy can also be used as a thermal maturity tool. WellDog has and is participating in various studies to determine how Raman thermal maturity results compare to other methods used. Initial results are very promising, and more work will certainly populate the database and bring enhanced confidence. Figure 8 shows spectra in a metamorphic progression from a low greenschist up to an extremely hot eclogite, where one can see that the disorder bands have completely disappeared. All that is left is the sharp G-peak. For the purposes of unconventional resource assessment what we would really like to do is pull this even farther back – out of that graphitization stage and into the diagenetic or carbonization regime.

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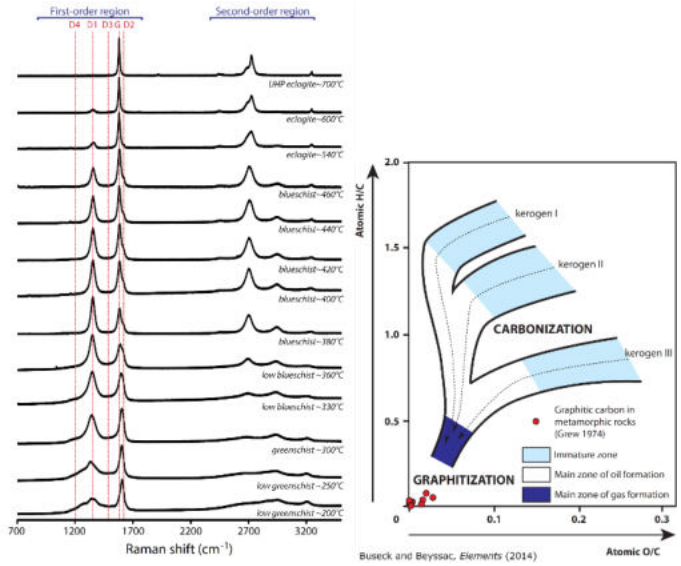

Figure 8. Left. Metamorphic progression of Raman spectra from a low-greenschist (~200°C) up to eclogite (~700°C). Right. Modified Van-Krevelen diagram showing the kerogen typing scheme and where the samples on the left fall on the scales.

Raman spectroscopy can not only determine the composition and quantities of the minerals present in the reservoir, but it can also get the total organic carbon (TOC) and thermal maturity. The next section describes the most commonly used current method of determining thermal maturity and then illustrates how Raman spectroscopy can help to attain a more accurate value.

Reservoir RockHound (RRH) – Laboratory Service – Know Your Reservoir Rock

Reservoir RockHound is a non-destructive lab service that can discern the minerals, microfossils, organic matter, and pore spaces (including its contents) in core, cuttings, plugs, or thin sections. It can also help determine thermal maturity.

Figure 9 shows how Raman spectra are acquired, and some resultant spectra. Samples are studied in a very methodical way either by a point scan, a line scan, or a grid scan. Using a grid provides a thorough analysis of the rock and its components and then various spectral maps can be created to show exactly the minerals that are present, including their location. This can lead to quantifiable mineralogic composition.

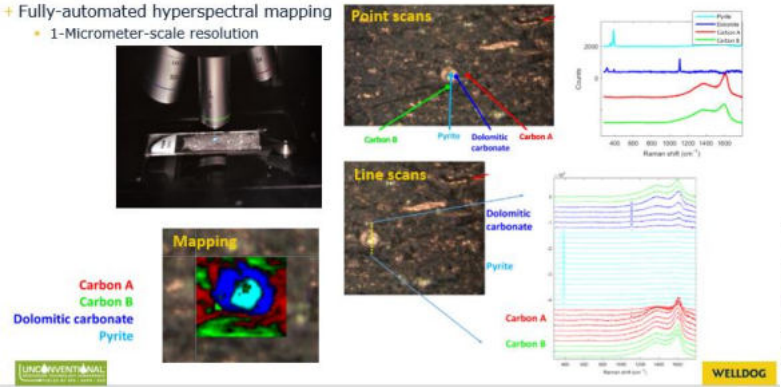

Figure 9. Photograph of the laser spot-focus onto the surface of a thin-section sample. Three modes of data collection are illustrated, including spectra from disparate point scans, spectra from a line scan across a feature, and a hyperspectral map

Figure 10. Optical view through spectroscopic microscope.

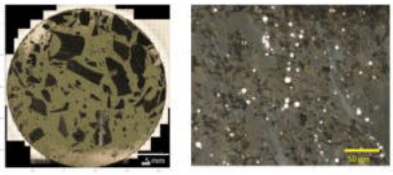

Figure 10 is an example of an optical mineralogic view through the spectroscopy microscope. A composite image on the left (each square is a single pass), and the photo on the right shows the highest resolution on the scope. Bright pieces in the photo on the right are pyrite (some rounder framboids). The stringy lighter gray color is the solid bitumen, maybe some inertinite. The rest is additional organic matrix material.

A hyperspectral map consisting of Raman spectra in every square micron over this region (about 200x300 square microns) can be collected and the data analyzed. Figure 11 shows a simple integration of the signal in the spectral window to capture several parameters. The first can be termed pseudofluorescence, and is a false-color map showing the range of fluorescence intensities.

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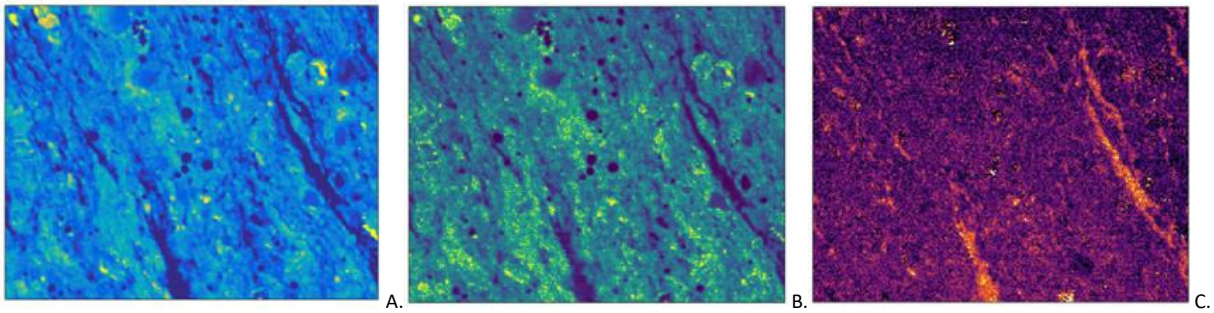

Figure 11. A. Pseudofluorescence. Higher fluorescence is yellow, lower fluorescence is blue. Pyrite is the darker circular shapes, bitumen streamers are also lower fluorescence and show up as darker streaks. B. Carbon Index. Again, pyrite and bitumen stand out in. Yellow denotes higher concentrations of carbon, perhaps denser; bitumen shows lower carbon, less dense. C. Looking at the G-cluster width (variations in the graphite peaks), the map starts to show different carbon types due to where the peaks are and how high they are. These variations allow the different carbon types start to come out.

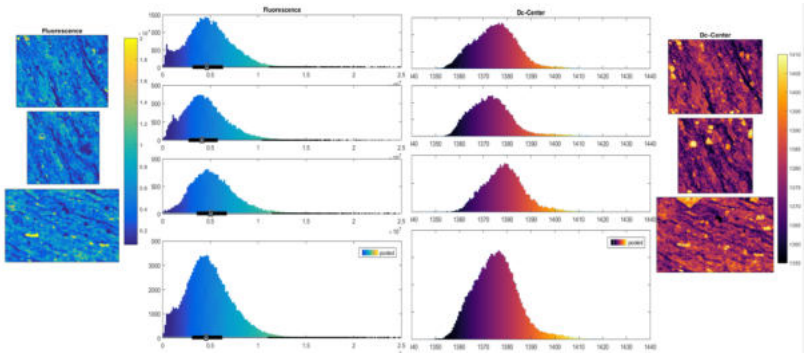

Figure 12. While Figure 11 shows separate maps of three different parameters from one sample, Figure 12 shows three different mapped areas, or sections, from a single sample, depicting variance throughout the plug.

A question often asked: how many minerals can really be differentiated? Literally thousands! Each different molecule has a distinct vibration style and frequency. Therefore, different minerals and polymorphs can be accurately determined by the resulting Raman, every time. This can be used to identify and quantify minerals and organic matter on a molecular vibrational basis. Since Raman is based on molecules and the arrangement of the molecular bonds, one can even tell the difference between minerals which have the same elemental composition. The polymorphs of titanium oxides and iron sulfides are easily distinguished in Raman spectra because the atoms in those crystals are arranged differently, and the vibrations are different (revisit figures 2 and 3).

Now not only do we know the fluids downhole, but we can also accurately describe the reservoir rock. Further, since we also know where the fluids are coming from, the reservoir composition from which they flow can now also be determined. What does that mean to the bottom line?

What can these data do for you?

How might these technologies benefit oil and gas exploration and appraisal? If the fluids in the well are known – composition, quantities, and where each is coming from – and the solids are also understood, exploration and appraisal teams can more accurately determine which zones to target within the reservoir. Further, reservoir, production, and drilling and completions engineers can understand the best places to stimulate in the well and which fluids might be most effective in the process, as well as in any future secondary recovery efforts. This can save millions of dollars, significant time and resources, as well as lead to more environmentally sound decisions and perhaps even better public relations. Armed with full knowledge of one's reservoir one can drill potentially fewer but more productive wells.

References

L. Taras Bryndzia*, Neil R. Braunsdorf & Ronny Hofmann (Shell International E&P Inc.), Quentin Morgan, Peter Christian, Art Toews, Jeff Parkins, Grant Myers & John Pope (WellDog, Laramie, Wyoming, USA). (2016). **Down-Hole Reservoir Raman System: A Novel New Technology for the Rapid Appraisal of Shale Gas Resource Potential.** Unconventional Resources Technology Conference (URTEC). #2431773