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THE VACA MUERTA PORE STRUCTURE AND ITS RELATIONSHIP TO OTHER UNCONVENTIONAL RESERVOIRS

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RESUMEN

La Formación Vaca Muerta, al ser una roca reservorio del tipo no convencional, presenta un sistema poral complejo que requierede una variedad de técnicas para describirla adecuadamente. La adsorción subcrítica de gas nitrógeno (SGA-N2) y la microscopía electrónica de barrido de emisión de campo (FE-SEM) se combinaron para obtener gráficos de distribución de tamaño poral para todo el rango de tamaños de poro en Vaca Muerta (~1.7 nm a 16 µm). El análisis SGA-N2 demuestra que la naturaleza de la porosidad alojada en la materia orgánica(MO) en Vaca Muerta cambia tanto vertical como lateralmente a medida que la formación se encuentra en distintas ventanas de fluidos. Esta tendencia coincide con resultados previos de análisis de poro en otras cuencas. El análisis FE-SEMpermitió descubrir los grandes poros inorgánicos que son atípicos de la mayoría de las rocas no convencionales. Estos poros son demasiado grandes para sercapturadospor SGA-N2 por lo que los tamaños de estos poros fueron medidos por FE-SEM. El análisis FE-SEM segmentó los poros alojados en la materia orgánica de los poros inorgánicos y luego se creó la distribución del tamaño de poro total. A pesar de la riqueza de materia orgánica de Vaca Muerta, este análisis muestra que solo el 5% de las muestras presentan más del ~50% de la porosidad alojada en laMO, lo que es atípicamente bajo comparado con otros reservorios no convencionales. Esto se refleja en la dimensión fractal calculada a partir de los datos de SGA-N2, que es menor que los valores generalmente informados para otrosgas shales. La comparación con otros reservorios no convencionales muestra que Vaca Muerta es única debido a su gran cantidad de porosidad inorgánica, aunque su porosidad alojada en la MO se comporta de manera similar a otros organic shale plays.

INTRODUCTION

The measurement of porosity is an inherently important part of the analysis of any reservoir rock. Total porosity is used to calculate, among other things, the total volume of potential reserves, the estimated ultimate recovery (EUR), and the optimal placement of completion zones in reservoirs. Small changes in the total porosity can influence large decisions in the unconventional reservoir (UCR) world.

The use of subcritical gas analysis with nitrogen (SGA-N_2) is relatively new to the energy industry. Long used in many other industries, primarily to measure specific surface area (SSA) and modal pore size, SGA-N_2 analysis has seen more and more usage as a pore structure characterization technique in UCRs. Kuila *et al.*, (2012) demonstrated that the clay content of the rock controlled the pore-size distribution for rocks with low total organic content (TOC) and the organic matter (OM) served to block much of the fine porosity in the rock when it reached about 3 wt.%. This lack of fine porosity in organic-rich rocks was due to the low thermal maturity of the OM that had yet to create much of its own porosity. The relationship of thermal maturity and the pore structure was described in detail by Kuila *et al.*, (2014a) in a study of a black shale at the base of the Baltic Basin. In this work, rock samples were measured by SGA-N_2 in both their as-received state and after removal of OM by sodium hypochlorite (NaOCl). The pore-size distributions were compared and divided into three groups based on the relative behavior of the distributions and the thermal maturity of the OM (as determined by the hydrogen index, HI). These groups will be discussed in more detail in the methods section.

The SGA-N_2 method of determining pore-size distributions has since been combined with otheranalytical methods to investigate the pore structures of some UCR rocks, primarily gas shales. Wang *et al.*, (2015) compared SGA-N_2 with CO_2 adsorption and mercury-intrusion porosimetry (MICP) to investigate some lacustrine gas shales and determined the primary porosity to be hosted in pores smaller than 100 nm in diameter. Chen*et al.*, (2016) combined the method with FE-SEM to characterize the relationships between pore size and type in nine (9) gas shales. Most recently, Yang *et al.*, (2016) used both SGA-N_2 and Field Emission Scanning Electron Microscopy (FE-SEM) to investigate gas shale samples. In this study, the fractal dimensions of the fine pores were calculated and limited differences were discovered in the two rock types analyzed. The fractal dimensions of gas shales had previously been measured by ultrasmall-angle X-ray scattering (USAXS) by Lee *et al.*, (2014). Most of the studies using the gas adsorption methods have used gas shales with high OM content, which hosts most of the porosity.

The Vaca Muerta formation in the Neuquén Basin of Argentina presents challenges in pore structure analysis that are not typical of gas shales. Gas shales tend to have the majority of porosity housed in their OM without a large inorganic pore component. Crousse *et al.*, (2015), Elias and Gelin (2015), and Reed *et al.*, (2017) demonstrate that the Vaca Muerta pore system varies significantly across the basin and with depth. Two primary factors contribute to this: 1) the thermal maturity of the OM varies greatly laterally and vertically (Fig. 1) and, 2) the stratigraphy consists of a laundry list of rock types from shales to marls to sandstones, some of which contain primary organic source rock and other that have been infiltrated by moveable hydrocarbon (Stinco and Barredo, 2014).

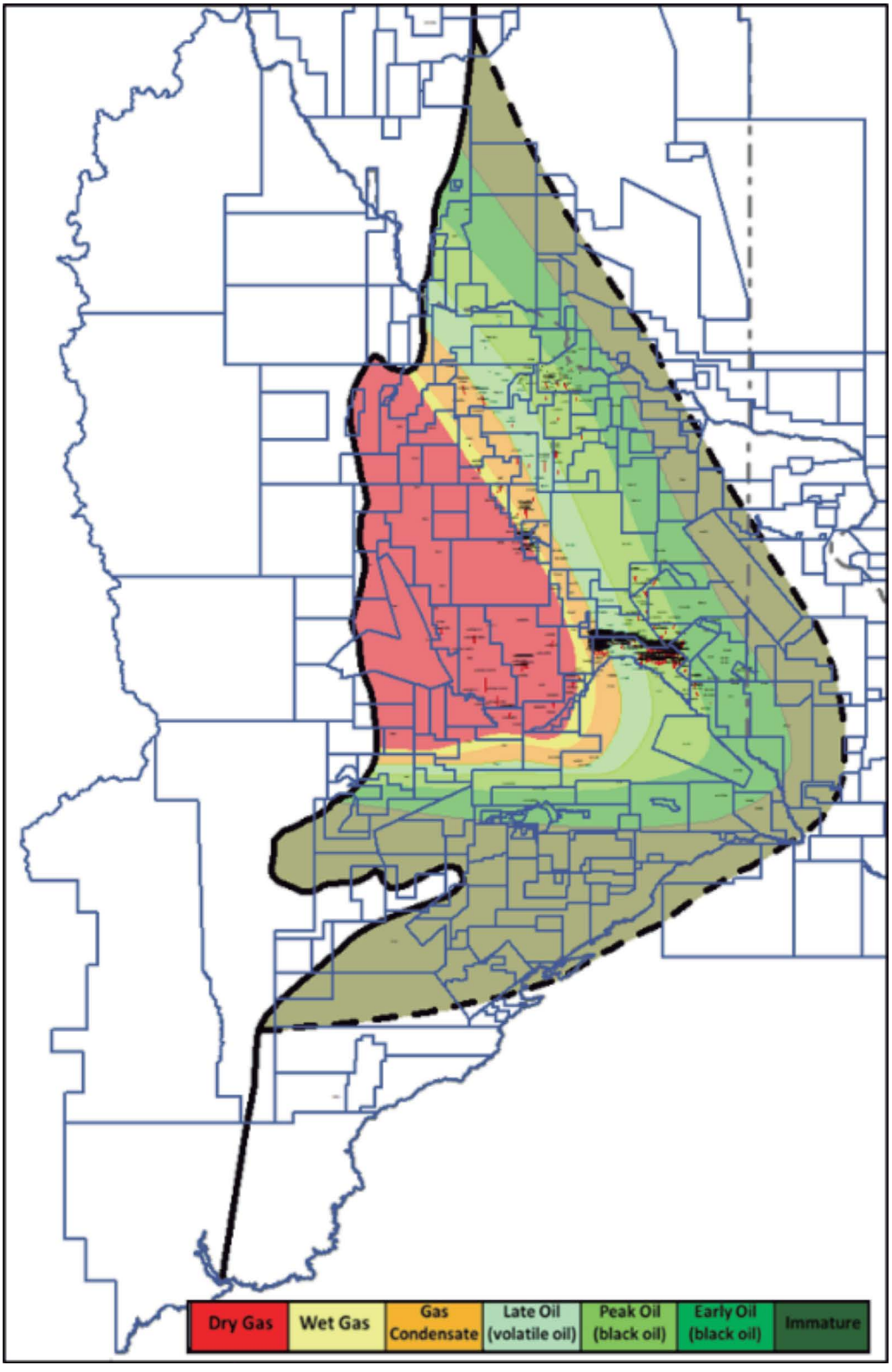

Figure 1. Thermal maturity map of the Vaca Muerta in the Neuquén Basin. OM content varies significantly across the basin and with depth within a development area.

In many respects, the Neuquén Basin is similar to the Baltic Basin studied by Kuila *et al.*, (2014a). Both basins contain similar amounts of OM, with an increase in thermal maturity laterally. However, the rapid lithification of the Vaca Muerta allowed large inorganic-hosted pores to remain. Further complicating the matter, some of the OM seated in inorganic pores is secondary bitumen that has infiltrated the larger inorganic pores and may have its own porosity. Liu *et al.*, (2017) used both SEM and reflected light micrscopy to measure pores with increasing thermal maturity and concluded that not only does the thermal maturity matter in the determination of OM porosity, but also the maceral type. Loucks *et al.*, (2012) attempted to catalogue the various types of pores in mudrocks, but did not apply a quantitative rigor to the analysis. However, the quantification of pore types and pore structure on multiple scales may be what is necessary to draw significant conclusions froma pore structure analysis. Jarvie *et al.* (2015) posit that oil in inorganic porosity will be easier to produce because of the decrease in surface sorption of the oil molecules through the formation. This is only true in cases where the surficial interactions between the surface and the fluid molecule impede movement, which depends on the difference in surface energy of the pore and the fluid molecules. However, a necessary first step in untangling the movement of fluids through pores is a full, quantitative description of the pore structure at all scales over which the pores exist in a reservoir.

This paper will present such pore-size distributions (PSD) combining the SGA-N_2 PSDs with PSDs obtained from FE-SEM. SGA-N_2 data was collected from 141 natural and OM-removed sampleacross three (3) development fields in the Vaca Muerta. For a subset of 56 samples from the most recent development field, FE-SEM pore-size distributions were made and analyzed side-by-side with the SGA-N_2 data. While this is not a new idea, the approach was significantly different than previous research. Where previous porosity image analysis has been completed focussing on the smallest of pores on small scales, the FE-SEM pore analysis and quantification here was completed on large-scale FE-SEM images, which were composites of multiple smaller-scale images. The full pore-size range could be measured on a large area of sample, reducing sampling bias and improving scalability.

The results obtained are in use to attempt to correlate the pore structure to log data, electro-facies, and producibility, which will be discussed in the companion paper from Crousse *et al.*, (2018). We will also compare the SGA and SEM results from the Vaca Muerta to several other UCR formations to attempt to place the Vaca Muerta UCR pore structure in a global perspective.

METHODOLOGY

A total of 141 samples were analyzed for their PSD between 1.7-200 nm by SGA-N_2 analysis. These samples were from both conventional core (CC) and rotary sidewall cores (RSWC) from

eight (8) wells in three (3) separate development areas. Of these, 134 were analyzed after treatment by NaOCl to remove OM content. While FE-SEM images were obtained from all samples over the three (3) fields, large-scale FE-SEM and pore size analyses were conducted on only the most recent 56 samples from two sets of RSWC samples from two (2) wells. Along with the analyses described here, a full suite of rock characterization analyses was performed including quantitative phase analysis by XRD, RockEval pyrolysis, retort porosity and saturation, and Water Immersion Porosity as described in Kuila (2014b).

SUBCRITICAL NITROGEN GAS ADSORPTION (SGA)

Subcritical Nitrogen gas adsorption (SGA-N_2) is a pore structure and surface area measurement that takes advantage of the Lennard-Jones potential minimum of a free gas molecule's free energy that exists on the surface of a solid. To make this measurement, surfaces of a sample must be cleaned by heating in a vacuum and then exposed to a gas. The differential pressure of the gas exposed to the surface is measured over time and the amount of gas adsorbed at each pressure is calculated. This is completed for a series of pressures up to the critical pressure of the gas at the specified temperature. In the case of nitrogen gas, samples are measured at the temperature of liquid nitrogen (LN) at atmospheric pressure, or 77K. Because of this low temperature, the method does underestimate specific surface area (SSA, De Jonge and Mittelmeijer-Hazeleger 1996) in low-maturity organic matter and, therefore likely the fractal parameter. However, there are several advantages to using N_2 gas over CO_2 gas for measurements in UCR rocks. The CO_2 adsorption method has a maximum pore size analysis value of a few nm, whereas N_2 can measure pores up to ~200 nm. This gives N_2 measurement an advantage for measuring the majority of pores that contribute to the overall pore structure of a UCR rock.

The measurement of the Vaca Muerta samples was completed on a Micromeritics ASAP 2020 or 2420 surface area analyzer. Approximately 1 g. of sample was de-gassed on the instrument at 200°C for 24 hours until the outgassing rate was <2 mmHg/min over a 10-minute interval. A full adsorption and desorption isotherm was measured, although only the adsorption isotherm was used to interpret the results. For a full discussion on why this is the case, please refer to Kuila *et al.*, (2012). The isotherm was then inverted using the Barett-Joyner-Halenda (BJH) method that assumes cylindrical non-connecting pores.The Harkins-Jura thickness equation was used to calculate the multi-layer adsorbed volumein the BJH inversion. While the choice of the BJH inversion and H-J thickness equation may seem arbitrary, the choice was made for consistency of all samples made in the Chevron laboratory, as our interest lies in being able to make comparisons between samples in a well, wells in a development area, development areas in a basin, and basins in the world. Consistency of analysis is important because the relative pore volumes change based on the thickness

equation used (Kuila *et al.*, 2012). SSA values were obtained by inverting the isotherm using the Brunauer-Emmert-Teller (BET) method (Brunaur *et al.*, 1938).

After measurement in their natural state, each sample was treated with 100 mL of a 6% sodium hypochlorite solution adjusted to a pH of 8.5-9.0 and stirred for 2h between 60-70 °C. The samples were then washed with deionized water and re-washed with NaOCl. The samples were then dialyzed to remove excess salts. As Kuila *et al.*, (2014a) explain, the procedure removes pyrite as well as OM, but all other phases remain intact.

After analysis, the PSD data for both the natural and OM-removed split is plotted as dV/d(logD) vs. pore size (Fig. 2). It is important to plot the differential pore volume because the size of the pore-range plotted varies greatly over the two orders of magnitude in the plot. Plotting simply volume with equally-spaced pore volumes presents a skewed graph that is dependent on wherethe measurement steps occur and not on the realistic pore size distribution.

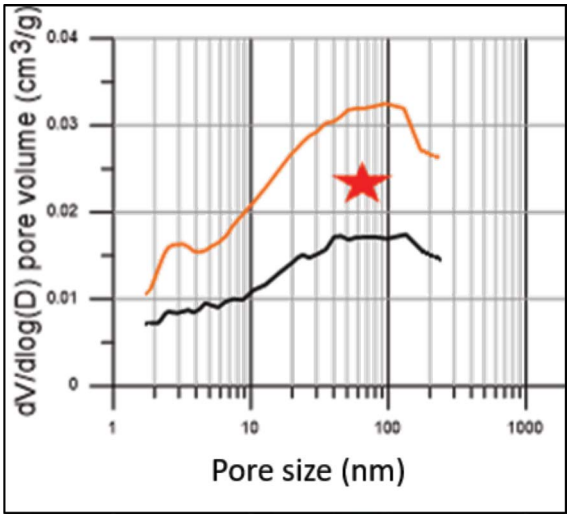

Figure 2. SGA-N_2 pore size distribution of one sample showing its PSD in the natural state (black) and the PSD in the OM-removed state (orange).

The pore-size distribution plot shown in Fig. 2 is typical of what Kuila *et al.*, (2014a) described as a Group 2 rock, where the porosity increases after OM removal along the entire pore-size range (In Kuila *et al.*, 2014a, the rock groups were labeled A, B, and C. We are using 1, 2, and 3 to maintain consistency with Crousse *et al.*, 2018). This is true if and only if the OM does not have a large amount of intra-granular porosity. Upon OM removal both large and small inorganic porosity is opened and the structure of the organic-free matrix is revealed. The sample in Fig. 2 shows a pore mode at 3nm, characteristic of clay porosity (Kuila *et al.*, 2012).

An example of Group 3 rocks is shown in Fig. 3 and is typical of rocks that contain mature OM with low HI values.

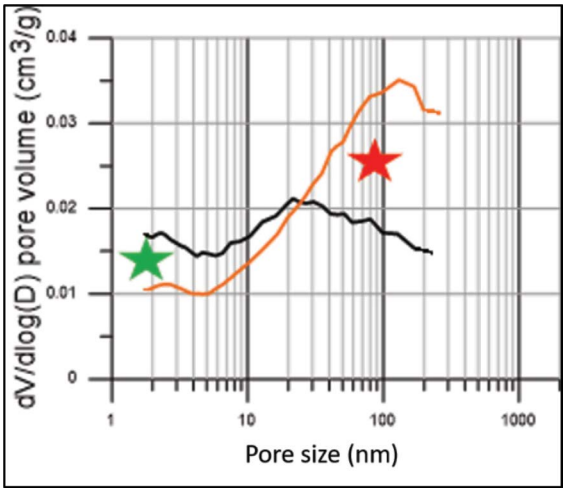

Figure 3. A Group 3 rock with thermally mature OM that contains significant small OM porosity. Upon removal of the OM, the small pores are removed (Green star) while the areas where the OM existed are opened (red star).

In the Vaca Muerta sample set, there were several that were difficult to classify as either a Group 2 or 3 rock, so a subset of samples Group 2-3 was added with characteristic decrease of small porosity after OM removal, but on a smaller scale than Group 3 samples (Fig. 4). In these samples, the decrease in the small pore size range are not as obvious as in Group 3 rock and this group has been created with the understanding that small pores may be created ordestroyed upon removal of OM. Therefore, it is difficult to determine the true causes of samples where the small pore volumes do not have an obvious change either positively or negatively.

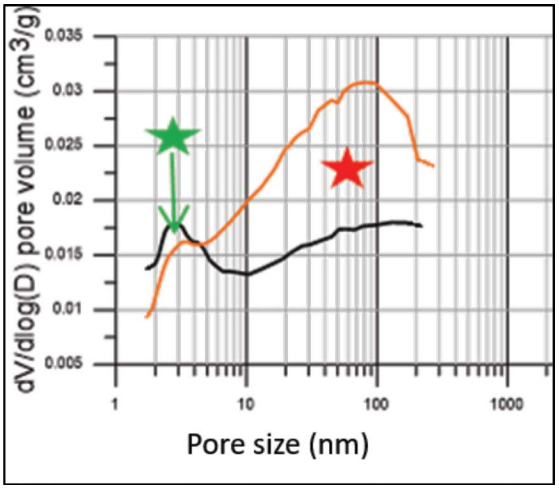

Figure 4. Group 2-3 rocks that show a slight decrease in the smallest pore-size region, but not as significant at the typical Group 3 rock. These rock types are typically situated stratigraphically between Group 2 and 3 rocks.

Two other parameters may be calculated from SGA-N_2 pore structure analysis, the specific surface area (SSA) or Brunauer-Emmert-Teller (BET) surface area (in m^2/g) and the fractal dimension, D, of the rock. For rocks that have numerous small pores, the SSA values tend to be larger than rocks that do not contain small pores. The fractal dimension of the rock is an intrinsic property of the rock's surface in situations where there is no regular or specified length scale (Mandelbrot 1983). The surface fractal number (D) can range between 2 and 3 is a measure of the irregularity or "roughness" of a surface. Values closer to 3 indicated more irregular surfaces and can be measured from SGA-N_2 isotherm data by the Frenkel-Halsey-Hill (FHH) formulation (Jaroniec 1995; Equation 1)

$$\ln\left(\frac{V}{V_0}\right) = constant + K\left[ln\left(ln\frac{P_0}{P}\right)\right] \quad (1)$$

Where the slope, K, is related to the fractal dimension by Equation 2:

$$D = K + 3 \quad (2)$$

Rocks with fractal dimensions close to 3 will have complex pore structures with high tortuosity. These pore structures may lead to more complicated fluid extraction.

Scanning Electron Microscopy (SEM)

Field-Emission Scanning Electron Microscopy (FE-SEM) images were collected on all samples that were analyzed by SGA-N_2 in all three development areas. Because of the nature of the porosity in the rocks, the SGA-N_2 pore-size distributions were inadequate to fully capture the complexity of the Vaca Muerta pore system. To account for the large inorganic pores that the Vaca Muerta contains, PSDs from FE-SEM images were made and compared with the SGA-N_2 PSDs in the third development area. In this area, using RSWCs, 56 samples were measured at both the small scale and the large scale by FE-SEM and PSDs were created by two typical methods (shape method and pixel method).

All samples were ion milled with a Leica Tix3X mill and then coated with 1 nm of iridium using a Leica ACE600 dual sputter coater equipped with a quartz crystal for measuring the coating thickness. Ion-milled samples were imaged under high vacuum in an FEI Quanta FEG-650 scanning electron microscope. Using FEI Maps software, automated runs were set up to collect 196 backscattered electron images on a thin-section size portion of rock using autofocus and no pixel overlap. Each image was an 8-bit image containing 2048 x 1768 pixels with an 8.86 nm pixel size. The total covered area for each large-scale composite was 254 x 219 µm. Each image dataset consisting of the 196 2-D images were transferred to an HP Z820 workstation for image analysis

using ImageJ (Rasband 2016). Images were loaded into ImageJ as 2-D image stacks where the pixel size and median filter was applied. Image segmentation was completed using the gradient method in a custom 3-phase segmentation plugin (Salazar-Tio 2012). The images can be segmented into pores, OM, and mineral phases based on the relative gray-scale intensity of each pixel (Fig. 5). A large-scale composite of the many small-scale images is shown in Fig. 6.

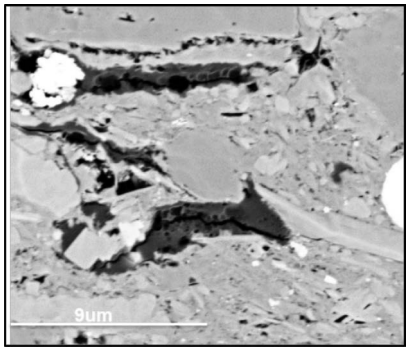

Figure 5. Backscattered FE-SEM image showing different elements of an image segmentation; pore (black), OM (dark gray), mineral (light grays), pyrite (white).

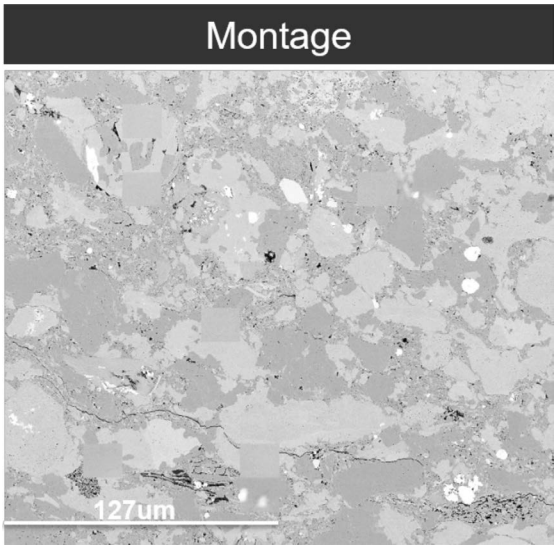

Figure 6. Large-scale montage of 196 images stitched together. The larger-scale allows the imaging of feature that may not be clearly noticed on smaller-scale images and gives a larger area of representation for analysis.

After segmentation, the image stack was converted to a large single image and the pores were delineated from the solid-phase material. To analyze the porosity and PSD, two methods were used: shape and pixel methods. In the shape method, based on the idea that organic pores tend to be more circular in shape than inorganic pores, all the pores in the large-scale image were measured and their circularity and roundness was calculated using Equations 3 and 4:

$$Circularity = 4\pi\left(\frac{Area}{Perimeter^2}\right) \quad (3)$$

$$Roundness = \left(\frac{4*Area}{\pi*major\ axis^2}\right) \quad (4)$$

All pores with a circularity of greater than 0.5 was considered an organic pore.

While this method may work for mature gas shales, with a large number of circular pores, the shape method did not coincide with a visual inspection of the pores in the Vaca Muerta. Some of the inorganic pores definitely met the circularity criteria for an organic pore and many pores in the organic material were elongated and more slit-like than round.

The second method for distributing pores into organic and inorganic subsets is on a pixel-by-pixel basis. The plugin used for this works by looking at any pixels in contact with a pixel that contains a pore and re-segmenting the pore based on the classification of the adjacent pixels. If the majority of the pixels surrounding a pore are classified as OM, then the pore will be classified as an OM pore. If the majority of the pixels around a pore are inorganic material, then the pore will be classified as an inorganic pore. After the re-segmentation of the pores, the diameters of the pores for the OM pores and inorganic pores are measured using the ferret diameters (long axis). These are then summed together to calculate the total porosity. Pore diameter and frequency measurements are transferred to a data analysis software to compute the histograms and PSDs

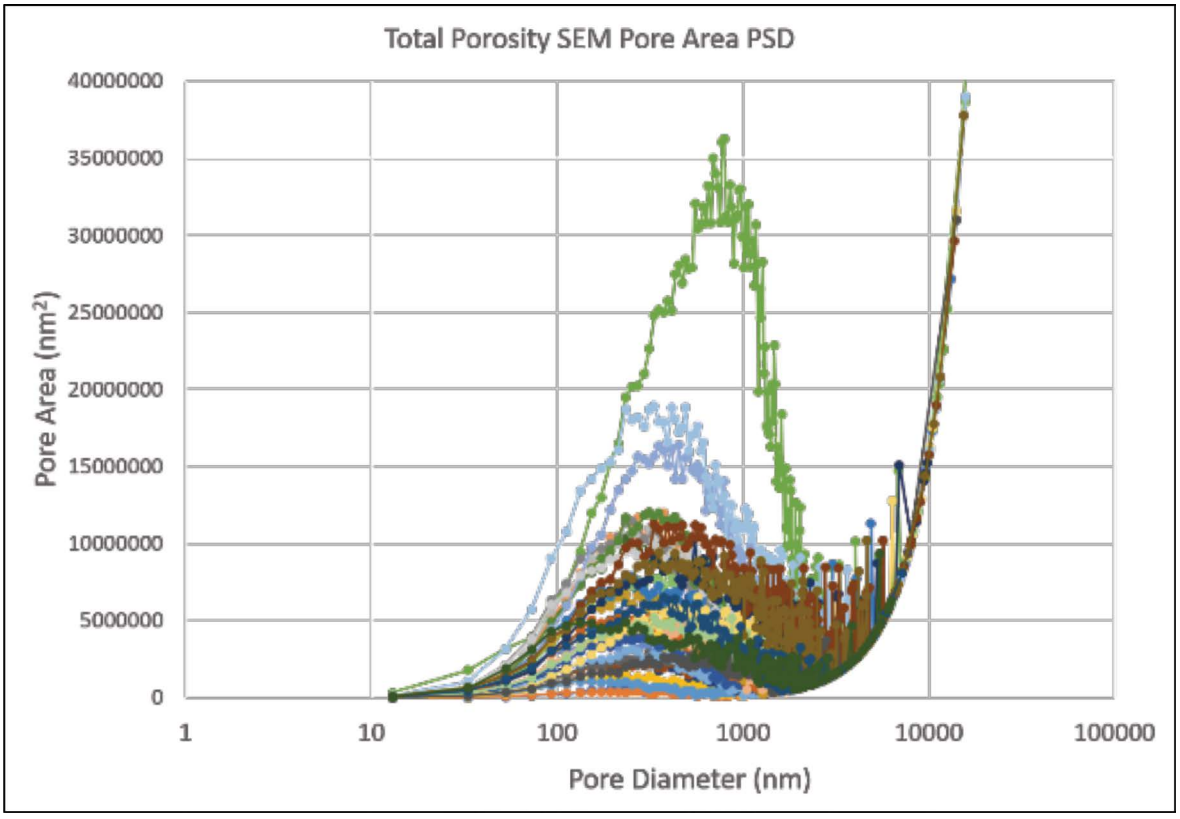

Figure 7. Pore-size distribution with equally-spaced bins.

using various criteria. This method is currently unable to distinguish kerogen (insoluble OM) from bitumen (soluble OM) or heavy oil, as they all have similar gray scales in SEM images.

An added complication of this type of analysis is the presence of induced fractures, either from the taking of the RSWC or the general preparation of the sample for analysis. To account for this, these fractures had to be removed from the image analysis. Because of the amount of automation in the image analysis, cutoffs needed to be applied to the pores to make sure the fractures were removed. After investigation of a large number of features that could definitively be called a fracture, the most appropriate cutoffs were determined to be a Circularity of 0.15 and a Roundness of 0.25 (Equations 3 and 4). Any pore that fell below both criteria was considered a fracture. These pores were then masked out of the analysis and not included in the PSD analysis.

The PSDs can be plotted in various ways and will show differences based on how the samples are binned. They can be binned in either equal-size bins or increasing-size bins and either based on the number of pores in each size or the area in each size. To determine the best way to represent the PSDs of the Vaca Muerta, all methods were tried. Ultimately, the most suitable method was

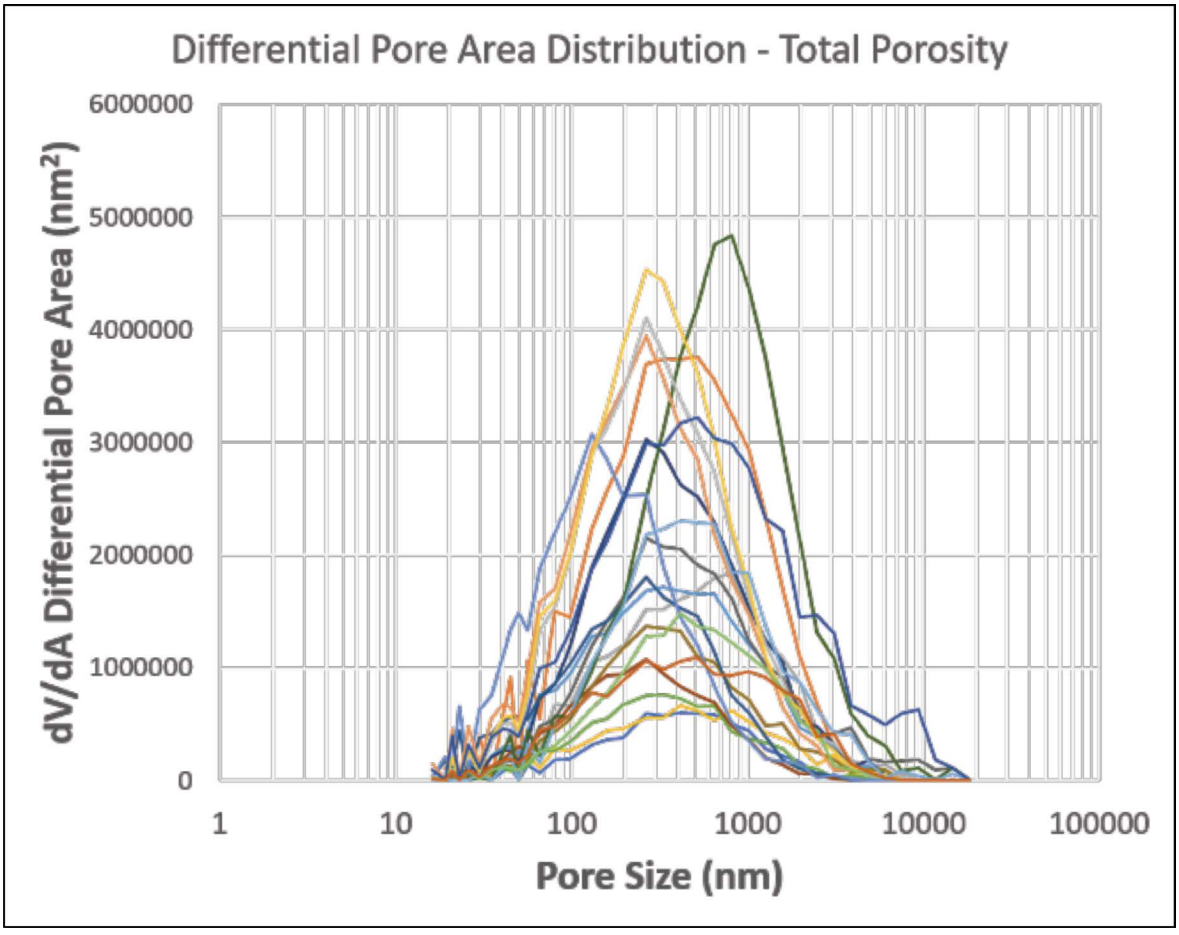

Figure 8. The same sample as shown in Fig. 7, plotted with geometrically-sized bins. The area plotted is a differential area that is necessary to avoid arbitrary effects based on bin size changes.

determined to plot pore areas binned in increments where each bin size was 1.25 times larger than the previous bin size. This was done because the PSDs from the SEM images were intended to be an extension of the SGA-N2 PSD plots, which have approximately that same ratio between bin boundaries. The different size of the PSD bins requires that a differential pore area dA/dD be plotted instead of the actual area within each bin. A PSD with equally-spaced bins is shown in Fig 7. This is inadequate for aesthetic purposes, but more importantly from computational purposes. When determining modal pore sizes, a single large pore may effectively dominate the PSD, due to its large area, even though it will not be an effective description of the pore structure of the sample.

Fig. 8 shows the same samples plotted with geometrically-shaped bins and the differential pore area. The two plots are mathematically equivalent, although the plot in Fig. 8 demonstrates the primary features of the pore sizes without the artificially large values at the larger pore areas seen in Fig. 7.

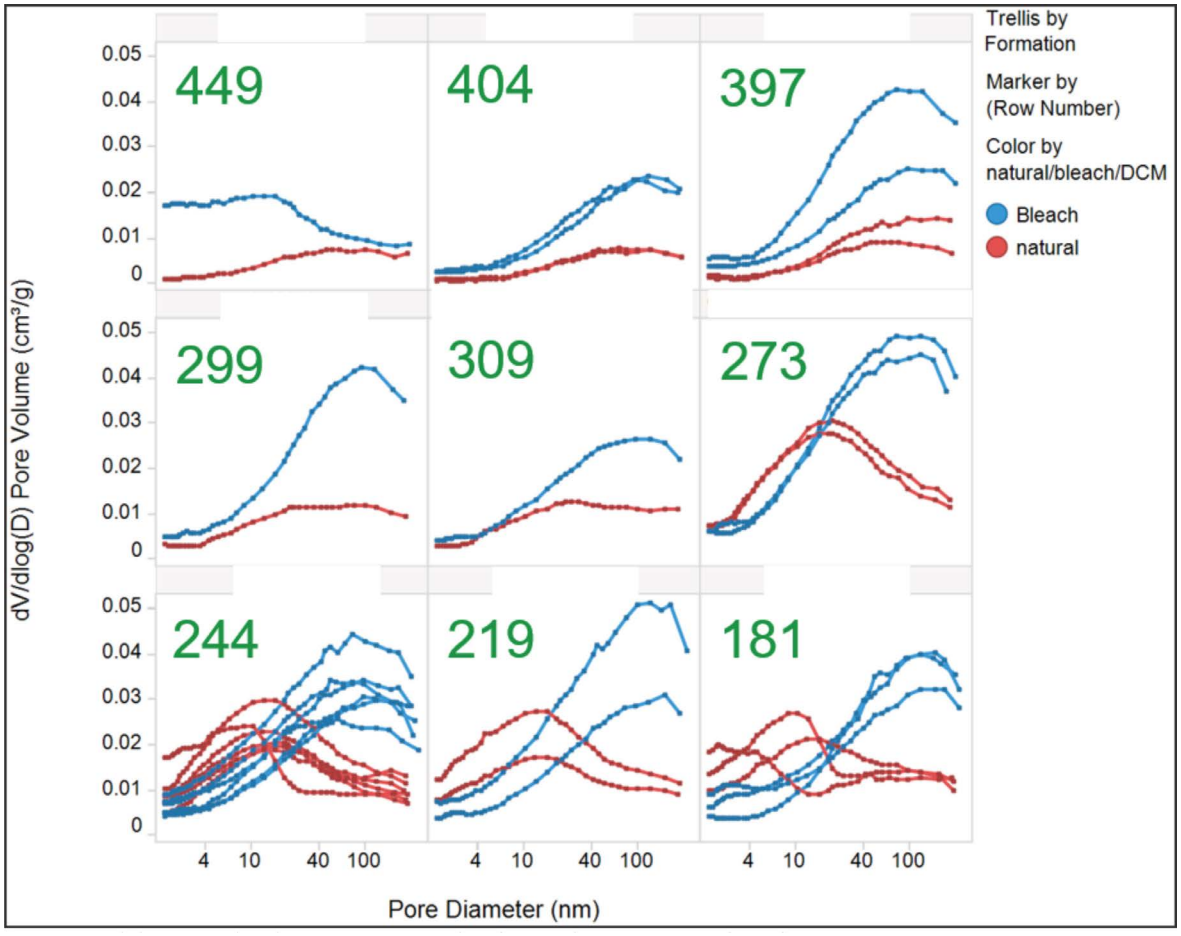

Figure 9. SGA-N2 PSD for both natural (red) and OM-removed (blue) samples in a Vaca Muerta development area. The depth is increasing to the right and down and the hydrogen index values, an indicator of thermal maturity are the numbers in green (lower values indicate more thermally mature OM.)

RESULTS AND DISCUSSION

Subcritical gas analysis was useful in distinguishing the fine pore structure changes both laterally and vertically in the Vaca Muerta. Fig. 9 shows a set of samples from one Vaca Muerta development area with increasing OM thermal maturity with depth. All the samples were analyzed in both natural and OM-removed states. As the thermal maturity increased with depth (indicated by decreasing hydrogen index), the fine porosity of the natural samples became more pronounced (plots in red below). Upon removal of the OM, the smallest pores were removed and large pores opened. This is indicative of the Group C rocks described in the Baltic Basin by Kuila *et al.*, (2014a).

This analysis was performed for all samples analyzed in the Vaca Muerta development areas and similar trends can be described in each one. The change in pore group can be tracked across a specific formation as the maturity of the rock changes from oil-prone to gas-prone.

The pores can be quantified by two methods, both the fractal parameter and the SSA. Fig 10 is a plot of the change in the fractal parameter of all the samples plotted with the thermal maturity of the OM (as indexed by HI). The fractal dimension of the rock increases significantly with the decrease in HI (increase in thermal maturity). This indicates a more tortuous path for a fluid through the samples and, usually, an increase in the surface area of the rock. In high thermal maturity rocks, with high fractal numbers and surface areas, the removal of the OM produced

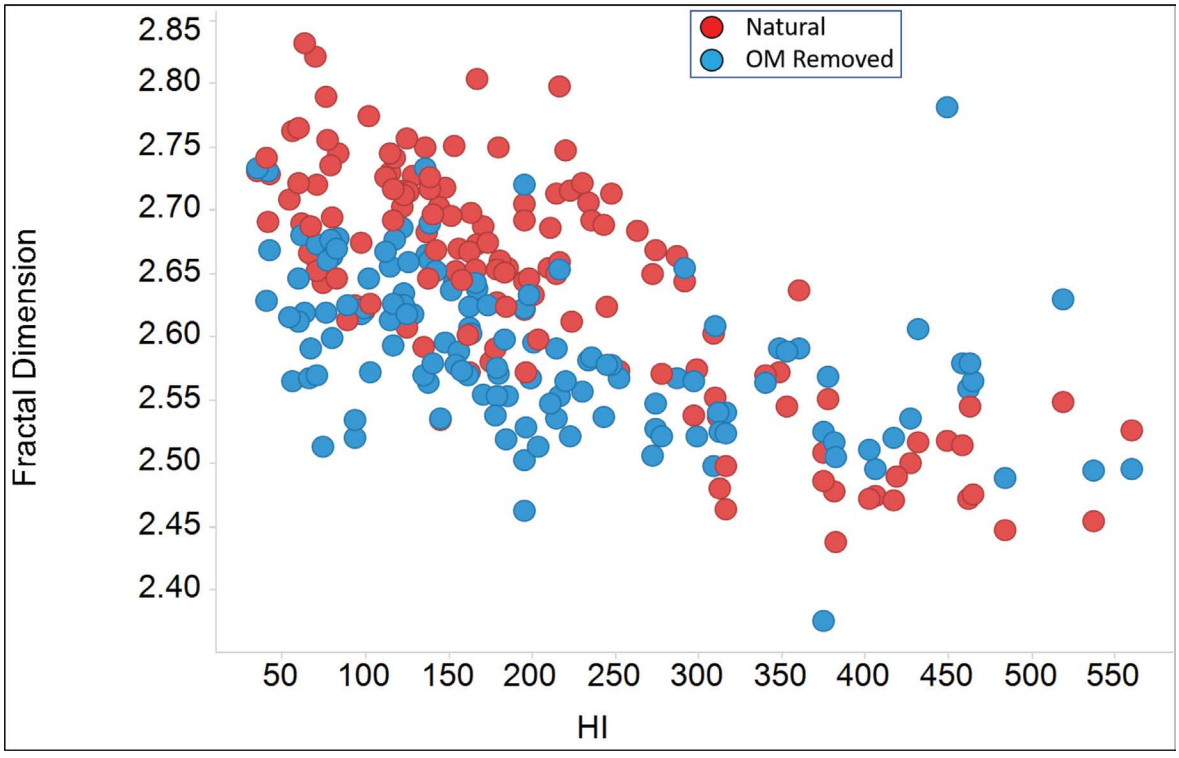

Figure 10. The Fractal parameter calculated from SGA-N2 isotherms for all Vaca Muerta samples. Samples in red are natural and samples in blue have had their OM removed.

lower fractal numbers, indicating that the inorganic matrix is a smoother, less tortuous pathway. However, in the low-fractal number, low thermal maturity rocks, removal of OM often led to an increase of the fractal number, which would indicate that the inorganic porosity is more complex than the OM porosity, perhaps due to a high amount of clay that has maintained its original complex structure that has not been altered by invasion of OM. The values of the natural rocks tend to never reach the high values reported by Yang *et al.*, (2016), which were measured on gas shales. This could be due to the significant contribution of the inorganic porosity that has lower fractal dimensions on its own than the whole rock.

One of the primary goals of this work was to determine a pore-size distribution for a set of Vaca Muerta samples from the smallest pores (~1.7 nm as measured by SGA-N_2) to the largest pores (up to ~16 μm as measured by FE-SEM). Fig. 11 shows the two PSDs of a Group 3 rock (left) and a Group 2-3 rock (right) with the SGA-N_2 PSD on top and the FE-SEM PSD on the bottom. The SGA-N2 PSD has both the natural and OM-removed PSDs plotted and the FE-SEM PSD is broken into total (black), OM (red), and matrix (blue) porosity plots. From the FE-SEM PSD, the inorganic porosity makes up the majority of the large pores, although the OM pores are prevalent at sizes that are larger than the SGA-N_2 method can measure. The Group 3 rock has a much larger number of small pores and OM-hosted porosity than the Group 2-3 rock. These can be compared with FE-SEM PSDs found in other areas in Figs. 14 and 15.

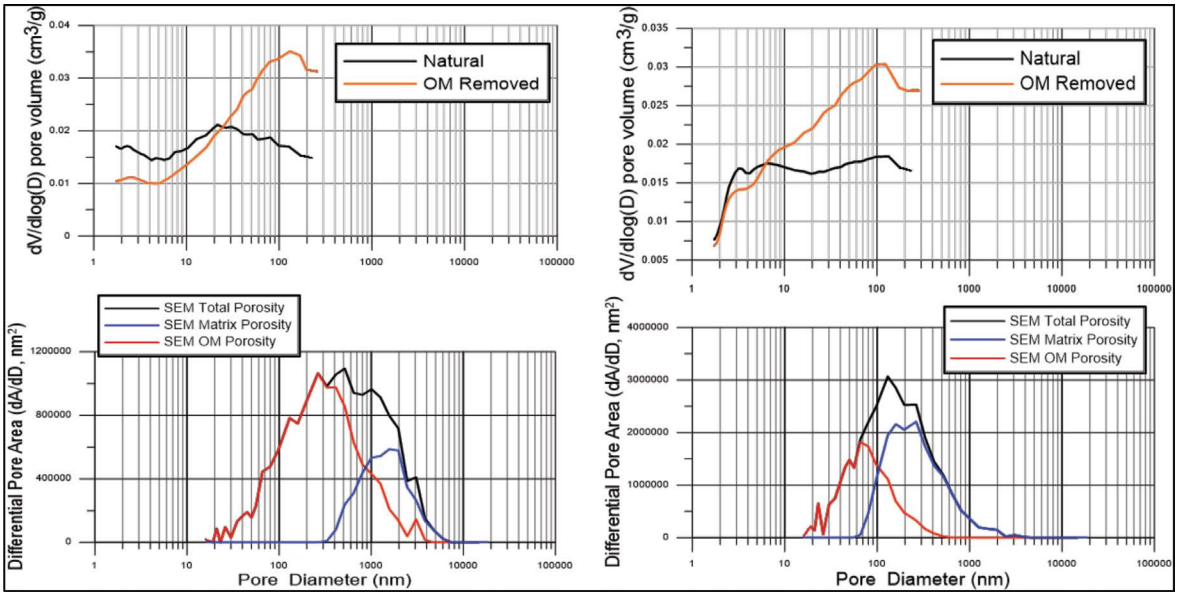

Figure 11. A combination of a Group 3 rock (left) and a Group 2-3 rock (right) with the SGA-N2 pore size distribution (top) and FE-SEM PSD (bottom) plotted on the same x-axis scale. Note the difference in y-axis.

The FE-SEM image analysis was used to determine how much of the porosity for each sample was hosted in the OM. The values range from 0.0% to up to 56.6% of the porosity. Group 2 rocks have an average of 6.4% of their porosity hosted in OM pores, Group 2-3 rocks have 24.7% and Group 3 rocks have 48.2%.

From these PSDs, various statistical methods can be applied that can compare the pore structures to other measurements including nuclear magnetic resonance (NMR), dielectric dispersion logs, and other porosity measurements. The goal is to then combine the data and correlate to electro-facies that can be used to find and/or predict the optimum production zones (see the companion paper from Crousse *et al.*, (2018) for a description of how the data gets further used.

THE VACA MUERTA FM. IN A GLOBAL PERSPECTIVE

A useful exercise in energy exploration and production is to compare established production areas to other potential production areas. Chevron over the past six (6) years has completed more than 1,000 SGA-N_2 analyses on rocks and have built a large library of PSDs from a large range of areas, some that are currently in production, some that may be, and some that were explored but not developed. SGA-N_2 PSDs for a selection of such areas are shown in Fig. 12.

The samples shown in Fig. 12 are from a range of rock types, as well as thermal maturity ranges. While gas shales tend to have a large volume of fine pores (Marcellus, Vaca Muerta and Baltic Basin), they need not always have some. A sample analyzed from a gas shale in China, for example, had no fine porosity development, despite its high thermal maturity. This sample's analysis

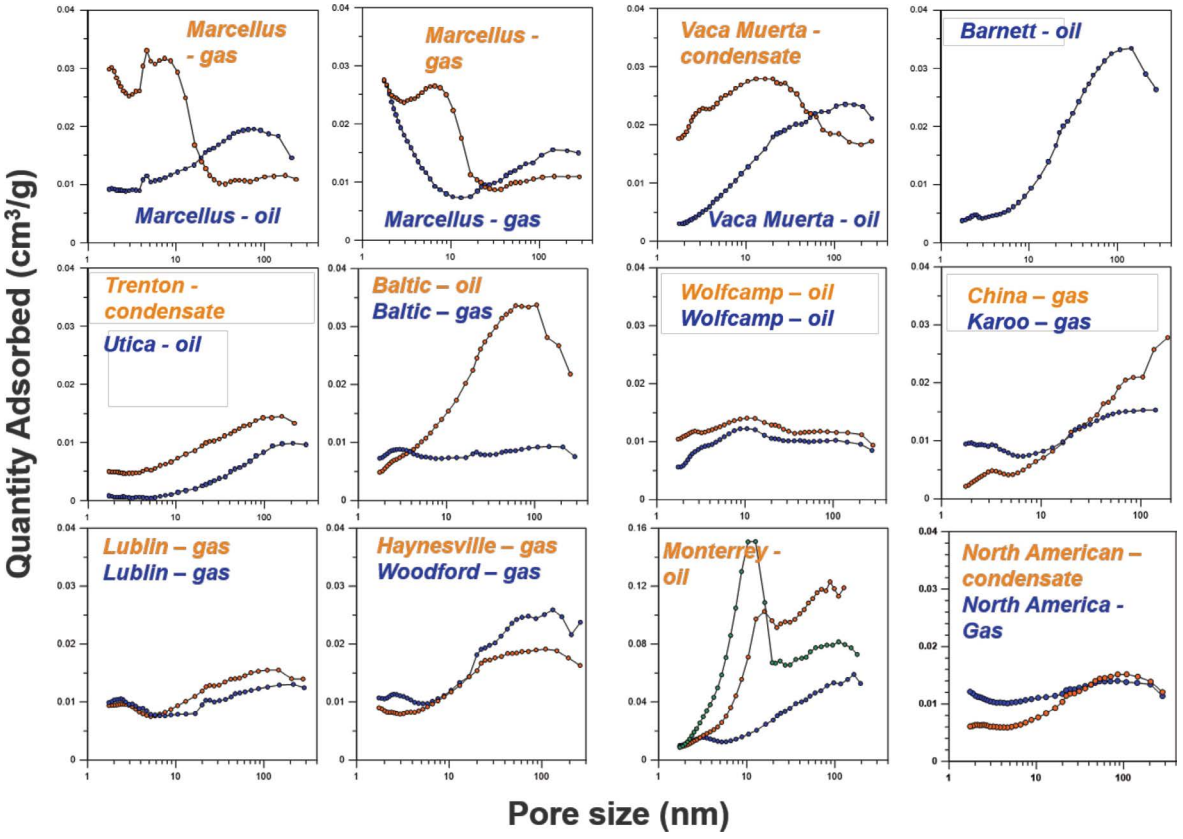

Figure 12. SGA-N2 pore size distributions from a selection of development areas worldwide. Note that all the y-axis scales are the same except for the Monterrey formation samples, which are on a much larger scale.

was hindered by the fact that it had almost no porosity at all, though. The message, then, is that all these analyses need to be used in context and with appropriate alternate measurement techniques. The overall trend, though, is clear – small pores tend to be created with increases in thermal maturity of OM in UCRs. The small porosity of the Vaca Muerta does not contain many more pores than other reservoirs. The main differences in the Vaca Muerta exist in the large, inorganic pores.

To further compare the Vaca Muerta with other rocks, we conducted the same FE-SEM pore size analysis on five (5) samples from other regions and different production profiles. The SGA-N_2 PSD shown in Fig. 13 is from a mature gas shale in the Marcellus formation. It displays the characteristic small pores of a gas shale and has a fractal parameter of 2.7353 and a SSA of 29.6 m^2/g. The highest measured surface area from a gas shale to date has been from the Marcellus and was measured at 56.9 m^2/g. For reference, pure clays (illite-smectite) can have surface areas up to ~120 m^2/g and pure, extracted kerogen has been measured up to 400 m^2/g.

The gas shale in Fig. 13 was also measured using the FE-SEM techniques described above. In many

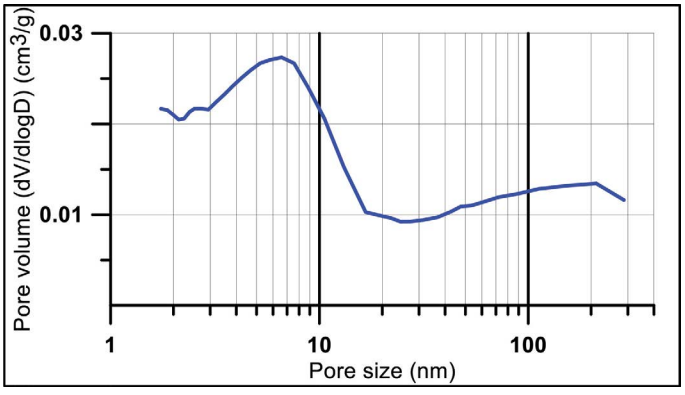

Figure 13. PSD from a mature gas shale from the Marcellus formation.

gas shales, much of the pore space is taken up by OM that develops its own porosity as the OM cracks and produces. Thus, the contribution to the porosity from the inorganic matrix often goes ignored.

Fig. 14 shows FE-SEM PSD for the total, OM, and inorganic portions of the Marcellus gas

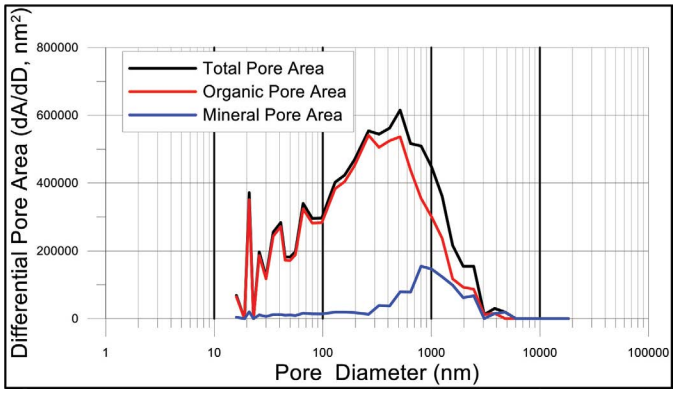

Figure 14. FE-SEM PSD analysis of a Marcellus gas shale sample.

shale. Note that, while the large majority of pores are hosted in the mature OM, not all the porosity is in the OM. Approximately half of the pores 1 µm in diameter are inorganic pores and even some of the smallest pores are not OM-hosted pores.

The FE-SEM PSDs of a Utica shale condensate samples and a Permian Basin oil-bearing formation were also measured (Fig. 15). The Utica shale sample has a similar profile to many of the Vaca Muerta samples, with a fairly significant amount of large inorganic pores. The Permian Basin sample, though, lacks significant inorganic porosity at any pore size. Also, an important feature to notice is that the y-axisscales of the Vaca Muerta and Utica samples are the same, whereas the Permian basin sample is about an order of magnitude smaller.

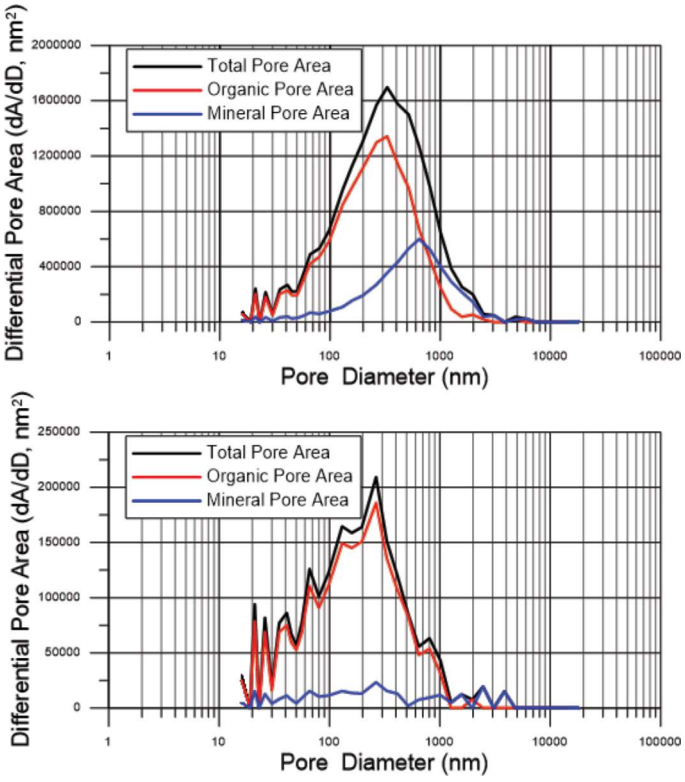

Figure 15. FE-SEM PSDs for a Utica shale condensate (top) and a Permian Basin oil-producing formation (bottom).

The Vaca Muerta has been known to have more porosity than many other UCR rocks (Crousse *et al.*, 2015). Much of that porosity is hosted in the inorganic matrix as opposed to the OM itself. The information in the combined SGA-N_2 and FE-SEM pore structure analyses will help to untangle the relationship of that to e-facies and production (Crousse *et al.*, 2018).

CONCLUSIONS AND FUTURE WORK

The Vaca Muerta pore system is unique in the UCR world. While the OM-hosted porosity of the reservoir behaves similarly to the analogous Baltic Basin, the Vaca Muerta contains significant inorganic-hosted porosity. Enough that even the most OM-rich and thermally mature samples form a development well contain at most 56.6% OM-hosted pores. When compared with samples from other important reservoirs, this is a small value.

The method of combining the SGA-N2 and FE-SEM analyses, while not a new idea, has been re-imagined here and completed in a way not previously published. The transformation of the FE-SEM image analysis into differential pore-size distributions emphasizes the contribution to the porosity of the formation from the inorganic portion. The Vaca Muerta porosity is greater than many other UCRs and this inorganic portion can account for much of that difference. It may also lead to better production over time, as it leads to a more open pore structure. The fractal parameter values that tend to be smaller than those reported for gas shales (Yang *et al.*, 2016) may be due to the significant inorganic porosity.

The relationship to facies and downhole logsis discussed in the companion to this contribution in Crousse *et al.*, (2018).

Although the pore structure analysis here has led to new insights into the Vaca Muerta pore system, improvement in the analysis can be made. Research into how to extrapolate 2-D images into 3-D pore size analysis is necessary. Focused ion beam SEM (FIB-SEM) can produce volume distributions that may be accurate over very small scales; however, the FIB-SEM technique is costly and it is inconceivable that an operator would pay for the number of analyses that need to be completed for the small sample sizes to have statistical significance. 3-D FIB-SEM is a useful tool in specific reservoir characterization, but has limited value in trying to scale up to larger areas. Part of the benefit of the work presented here is that the large-scale maps composed of 196 different small-scale segments overcomes the spatial limitation of the FE-SEM without sacrificing the small-scale resolution.

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