

# **Applications of Portable XRF, Chemical Stratigraphy and SEM in the Horn River Basin\***

**Thomas C. Weedmark<sup>1</sup>, Ronald J. Spencer<sup>1</sup>, Darren P. Juss<sup>1</sup>, and Francois Marechal<sup>2</sup>**

Search and Discovery Article #41279 (2014)

Posted March 10, 2014

\*Adapted from extended abstract prepared in conjunction with presentation at CSPG/CSEG/CWLS GeoConvention 2012, (Vision) Calgary TELUS Convention Centre & ERCB Core Research Centre, Calgary, AB, Canada, 14-18 May 2012, AAPG/CSPG©2014

<sup>1</sup>University of Calgary, Calgary, Alberta, Canada ([tweedmark@gmail.com](mailto:tweedmark@gmail.com))

<sup>2</sup>Quicksilver Resources Canada, Alberta, Canada

## **Abstract**

The Horn River shale sequence is thick and heterogeneous in composition. In order to achieve a profitable well, horizontal legs must remain within organic rich shale intervals exhibiting rock properties conducive to hydraulic fracturing. The nature of organic rich shale can make it difficult to recognize compositional changes through the conventional techniques of binary microscopy and natural gamma measurements. The introduction of portable XRF (x-ray fluorescence) instruments gives us the ability to quickly and accurately view compositional changes by creating chemical stratigraphy logs. Through SEM (scanning electron microscope) study of drill cuttings from a variety of chemical zones the fabrics and rock properties related to specific chemical compositions are inferred. The XRF instruments also make it possible to create logs during drilling operations and effectively steer horizontal legs into zones, which will yield greater production.

## **Introduction**

The Horn River play contains dry gas locked within tight organic rich shale. The compositional and mechanical properties of this shale change in both the lateral and vertical directions. In order to exploit this play effectively methods must be developed to maximize well placement with respect to reservoir quality and fracture potential. The introduction of portable XRF instruments allows for the construction of chemical stratigraphy logs for more than 25 different elements. These logs have a variety of applications in the areas of exploration, reservoir evaluation, drilling and completions.

## **Methods**

Samples consist of cleaned drill cuttings collected from two well locations in NE British Columbia; two pilot holes and three horizontal legs ([Figure 1](#)). Pilot holes are approximately 2,800m deep and pass through Late Devonian Horn River shale target zones before terminating in carbonates of the Middle Devonian Pine Point Formation. Cuttings were collected at 5m intervals for the pilot and build sections and at 10m intervals along the horizontal legs. Each sample was crushed into a powder using mortar and pestle in preparation for XRF analysis then placed in a specially designed sample cup. The portable XRF instrument must be calibrated to a set of known standards to ensure accurate elemental

measurements before any samples are run. Currently there are two modes, which are run for each sample to gain all of the relevant chemical data. The first is “Mining Mode” which takes 90 seconds and gives major elements related to the lithology of the rock (Si, Ca, Al, K, Fe, etc.). Next is “Soil Mode” which requires 135 seconds and provides a list of trace element concentrations (Mo, U, Th, Rb, Zr, Mn, etc.). The data for both modes are then transported to Excel for processing and construction of the chemical stratigraphy logs.

## **Data and Results**

Using the chemical data acquired through XRF, we developed four key data sets referred to as gamma, majors, trace, and structure. The gamma data set compares spectral gamma data from wireline logs against K, Th, and U concentrations gathered through XRF ([Figure 2](#)).

We are able to confirm sample depths and create pseudo-spectral gamma logs by overlaying the XRF data on the well logs. The XRF data are run through a simple low pass filter to reduce high frequency scatter caused by uncertainty in measuring elements with very low total concentrations. Once filtered, a multiplier for each curve is applied to the XRF values to produce expected gamma counts. The multipliers are adjusted in order to get the best match between the log data and measured data; the counts are added together to produce the Pseudo-Gamma curve. This enables us to build spectral gamma logs along the build and horizontal portions where conventional logging may not be feasible or practical.

The major data set is essential for locating desirable hydraulic fracturing targets within the shale sequence. Elemental concentrations are converted to oxides and sulphides then normalized to reflect  $\text{CaCO}_3$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeS}_2$  percentages within the rock ([Figure 3](#)). Using these percentages, we can clearly distinguish any lithologic changes throughout the section. We are able to pick out several carbonate markers above the Horn River shale in the Fort Simpson. These markers are important for accurately landing horizontals. There are five specific carbonate markers, which are continuous throughout this portion of the basin; C-1, C-2, C-3, Victoria Scarp (VS), and Marechal Horizon (MH). From a fracturing standpoint, there are two main contributing factors to brittleness, which are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  proportions. Higher  $\text{SiO}_2$  values tend to make the rock more brittle while higher  $\text{Al}_2\text{O}_3$  amounts generally have the opposite effect. We are currently in the process of linking specific chemical compositions to fabrics and both of these to Poisson’s Ratio values. Another application is in sequence stratigraphy as several orders of relative sea level cycles are apparent.

Several samples within the Horn River shale sequence having different chemical signatures were examined under SEM. The results show that certain chemical compositional ranges are indicative of specific shale fabrics ([Figure 4](#)). Sample 3085 (left) comes from a shale rich in aluminosilicates with no visible cements. Porosity is very low due to the soft compacting nature of this rock. This sample may have high a TOC; however, the composition and fabric make it unsuitable for hydraulic fracturing. If fractures are induced, the soft ductile nature of the rock will not allow them to remain open. Sample 3075 (middle) shows a shale with detrital fabric and a low degree of cementation. This rock has large organic fragments and a relatively high porosity. This type of rock will likely produce a network of fractures if hydraulically stimulated, with the ability to remain propped open. Sample 3065 (right) shows shale heavily cemented by silica, possibly from a hydrothermal source. This type of fabric has relatively moderate porosity and a high TOC. Fracture stimulation in this type of rock will tend to produce long and narrow fractures with the ability to remain open. Chemical composition is not unique to a specific fabric type; however, a specific fabric type will tend to fall within a certain range of normalized oxide compositions.

Sediments deposited through detrital means appear to show a constant ratio between  $\text{SiO}_2/\text{Zr}$ , in which the Si is converted to a normalized oxide and Zr is simply in ppm. Several intervals within our sample area are heavily cemented with silica. There is evidence in the Slave Point carbonates, adjacent to the Horn River Basin, that there were pulses of hydrothermal activity during the time of deposition. It is very likely that this hydrothermal activity extended out into the basin in the same way large faults within the carbonates extend into the basin. Silica cemented intervals also contain unusual minerals such as barium rich feldspar, monazite and iron rich dolomite. These minerals are not part of the deep basin detrital sediments. Instead, they appear to have grown in place and are surrounded by rings of organic carbon, which appears to have been pushed out during growth. Zones containing these minerals also show a general trend of high  $\text{SiO}_2/\text{Zr}$  ratios. Even slightly cemented samples have elevated  $\text{SiO}_2/\text{Zr}$  values when compared to samples with no cement. By comparing  $\text{SiO}_2$  and normalized  $\text{SiO}_2/\text{Zr}$  values against depth, zones, which are cemented through hydrothermal activity, are quite apparent ([Figure 5](#)).

The trace data set is a useful tool for locating organic rich shale, hydrocarbon potential and estimating redox conditions during deposition. This set consists of Mo, V, U, Mn, Cr, Ti and Ba concentrations ([Figure 6](#)) plotted against depth. Relative trends in Mo, V, U and Mn are used to locate potential targets. Work done on black shale in Australia suggests heavy contributions of Mo and V from marine bacteria and algae (Lewis et al, 2010). Organic matter from those organisms contains Mo, U and V; however when oxidization occurs the Mo and U ions return to seawater while V can lock into clay minerals such as diagenetic illite. Mo presence indicates reduced organic matter, but the concentrations can be influence by other factors such as hydrothermal activity, water ph, or sulphide abundance. U tends to correlate more proportionally to TOC, unlike Mo, and is therefore used as a proxy for organic matter. Since V sourced from organics is locked under both oxidizing and reducing conditions, its concentration can be related to organic production through time. Finally, the Mn concentration is very sensitive to changes in redox conditions because it is mobile when reduced and is locked when oxidized. These factors put together (elevated levels of Mo, V, and U with decreased Mn) are used to indicate a paleoenvironment where significant organic accumulation occurred under anoxic conditions. This results in the deposition of black organic rich shale.

Building chemical logs from XRF analysis also helps to determining structural features. Local bedding orientations are found by a simple depth comparison for specific markers between two build sections. This can also be done between build sections and the pilot hole. Chemical signatures from any combination of the three main data sets can be compared if clear patterns are present. For any clear correlation, the North/South and East/West apparent dip components are found using the survey data. Once several correlations from different depth ranges are made, an average for all the dip data is calculated. Using basic trigonometry on the two averaged apparent dips (N/S and E/W), the local true strike and dip is found. For the Horn River shale units in this area the local strike and dip was found to be to be  $033^\circ/4.4^\circ$  SE. Regional stratigraphy and structure can be determined using marker unit correlations between wells with significant separation. Chemical signature analysis used in conjunction with structural data aid in steering horizontals within the target zone.

Once a horizontal is landed in the target zone, the general dip of the bedding in that direction should be followed. To ensure the bit does not wander out of the target zone, distinct changes in concentrations for several elements above and below the target should be distinguished from the pilot hole samples. Any approach or penetration of those marker units is obvious and can be corrected for to maximize borehole placement in the target formation. In this study, a sample rate of 5m through the target zone, within the pilot hole, did not have good enough resolution to select markers needed for steering the horizontal. If samples are taken at a spacing of 1m continuously from 20m above through to 10m below

the target zone, then clear boundaries for the horizontal can be defined. This may slow down drilling operations for a short time during collection; however, it should save time and money when drilling and completing the horizontals.

### **Conclusion**

In conclusion, the availability of portable XRF instruments provides chemical stratigraphy data in a quick and inexpensive manner. The quantity of information gathered from this type of analysis is enormous, approximately 25-30 useable element readings per sample. This paper briefly touches on a few applications for these data related to the exploration and production of unconventional hydrocarbon reserves. By applying these concepts during drilling operations, operators can maximize the potential of each well and avoid waste related to poor horizontal placement and ineffective fracture treatments. As more XRF data are collected from wells during and post drilling, regional mapping of reservoir quality will be possible. As well, the ability to understand factors relating to differences in quality is fundamental such as hydrothermal cementing, clay content, and rock fabrics. Chemical stratigraphy also allows sequence stratigraphy to be performed in the subsurface with a higher degree of accuracy. This is especially true for shale and siltstone units where changes in lithology are difficult to determine through traditional methods.

### **Acknowledgments**

I would like to thank Alberta Innovates Technology Futures (AITF) for supplying me with the lab space and equipment to conduct this research. I would also like to thank Quicksilver Resources Canada for providing drill cuttings, well logs, and the other research materials required to complete this project.

### **Reference Cited**

Lewis, S.E, R.A. Henderson, G.R. Dickens, G.A. Shields, and S. Coxhell, 2010, The geochemistry of primary and weathered oil shale and coquina across the Julia Creek vanadium deposit (Queensland, Australia): Mineralium Deposita, v. 45/6, p. 599-620.



Figure 1. XRF Analysis. The procedure for performing XRF analysis is relatively simple. Drill cuttings are crushed in a mortar and pestle then placed into a special XRF sample cups provided by Chemplex. Each sample is run through “mining” and “soil” modes on the Innovex X-5000 portable XRF unit. It takes roughly ten minutes to crush and run a sample through both modes.

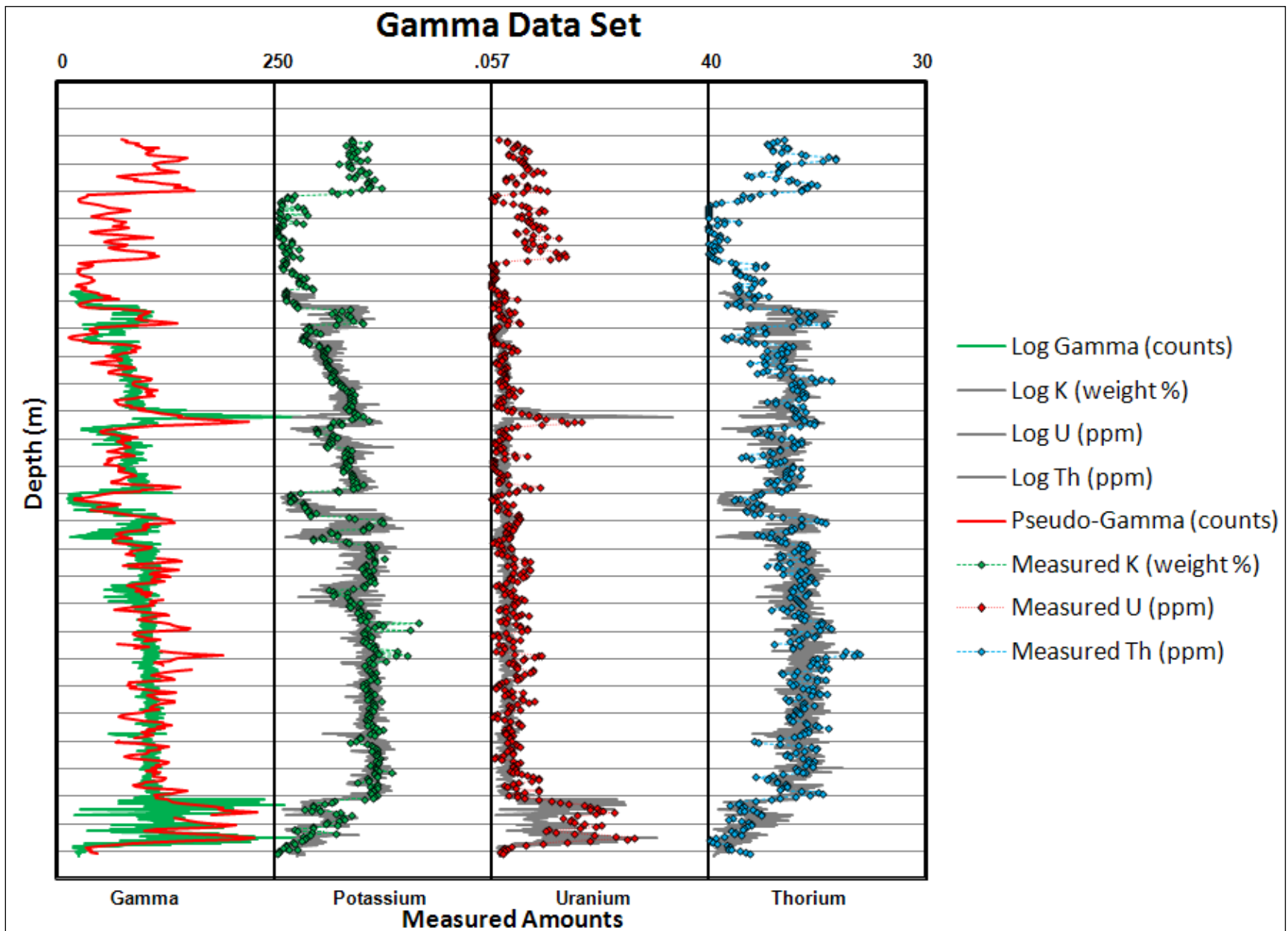


Figure 2. XRF and Log Gamma Comparison. Depth markers have a spacing of 100m.



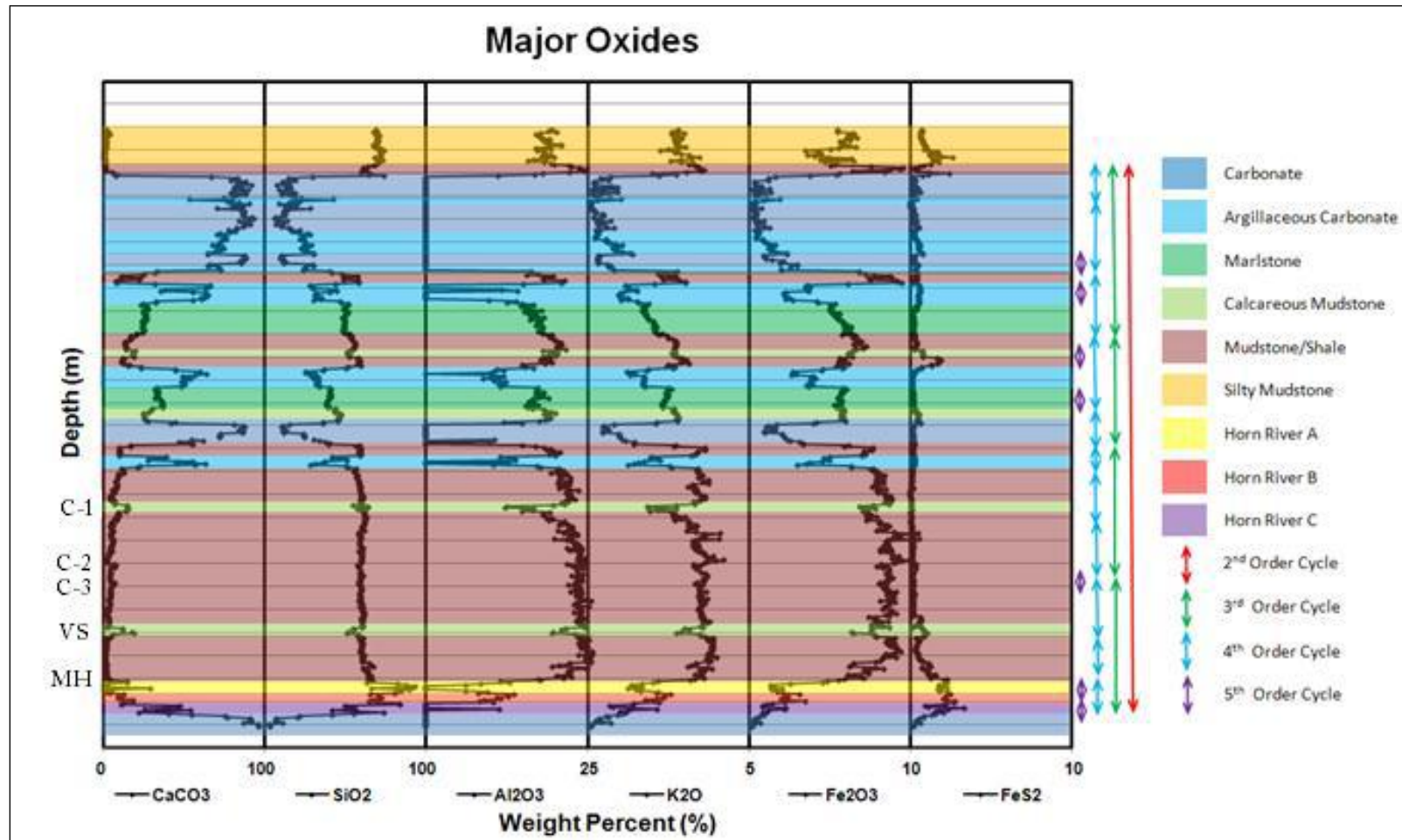


Figure 3. Normalized Major Oxides. Trends in oxide percentages make it possible to interpret changes in lithology from top to bottom. Sequence stratigraphy has been applied to the interpreted lithologies. One full cycle is designated as one HST to the next HST. The HST is marked by the top of the deepest relative sea level unit. The overall shallowing upward sequence appears to be part of a 2nd order cycle from the Devonian to the Carboniferous. It appears that up to 5th order cycles can be discerned at this resolution. Within the Horn River shale units the most brittle (possibly most cemented) interval is Unit A. Unit B appears to be quartz rich detrital shale with increasing carbonate content and small degree of cementation. Unit C is predominantly a marlstone with abundant carbonate debris flows and quartz rich detrital silt/shale layers. Each depth marker has a spacing of 100m.

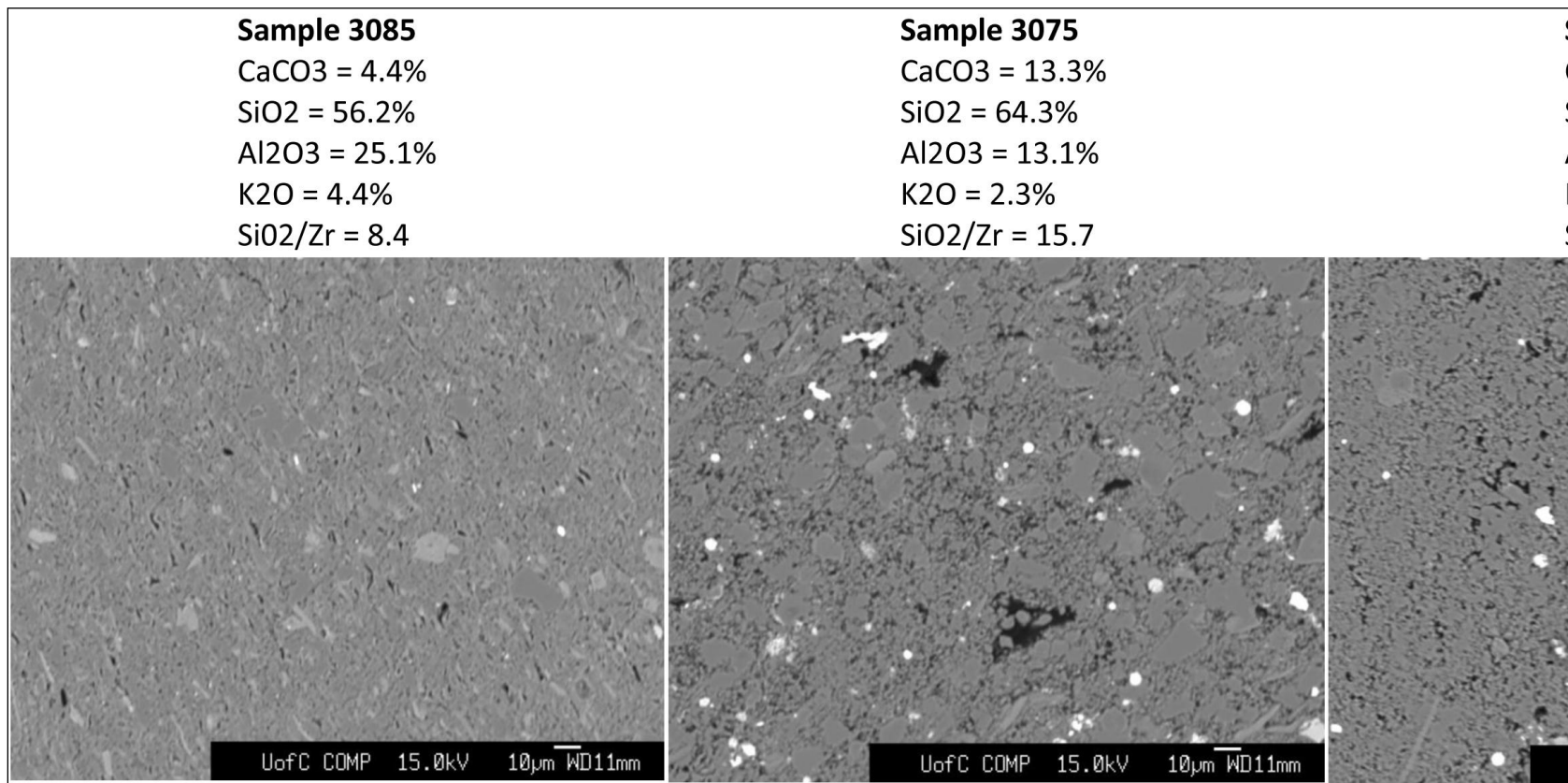


Figure 4. SEM Images of Shale Fabrics. All SEM images created from drill cuttings set in epoxy and polished.



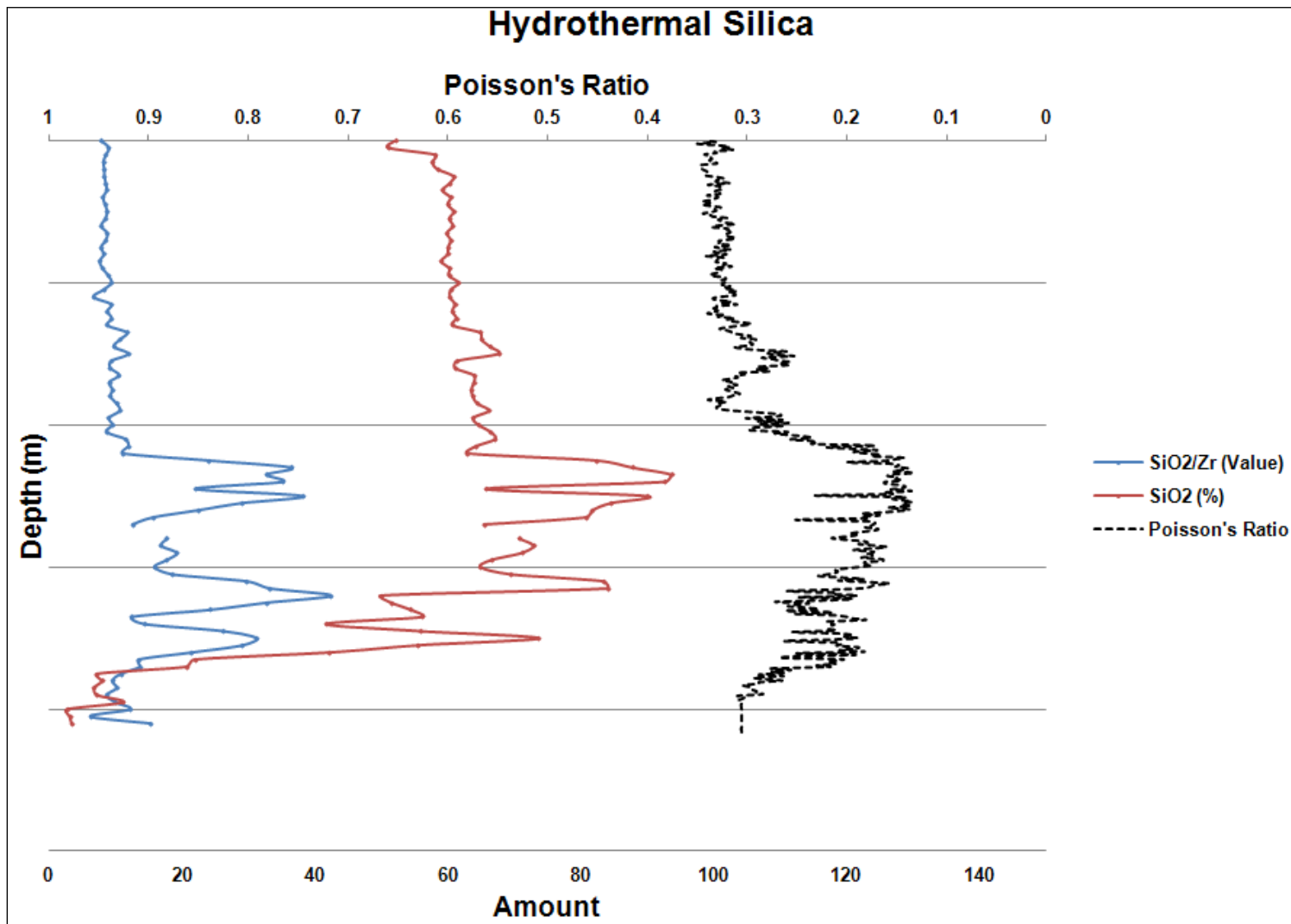


Figure 5. Relation of Composition and Shale Fabrics. A zoom in of the Horn River shale, each depth division is 100m. Large spikes in SiO<sub>2</sub> concentrations coincide with spikes in the SiO<sub>2</sub>/Zr ratio. When compared to SEM analysis, these spikes appear in zones, which tend to be well cemented and brittle.

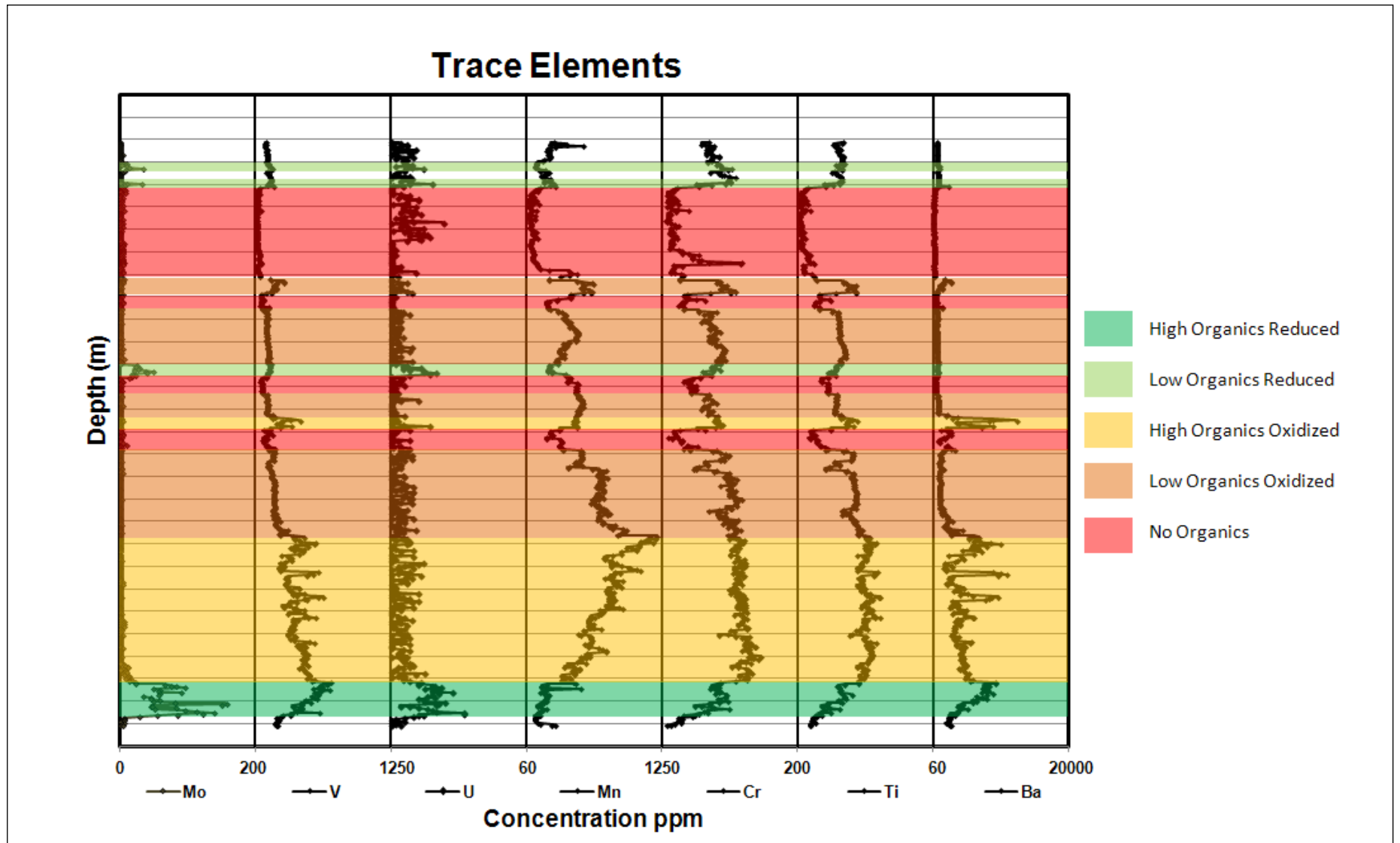


Figure 6. Trace Elements. The Horn River shale has a high TOC and was deposited under anoxic conditions. In this area, there are increased concentrations of Mo, U, and V with a decrease in Mn. When these same parameters are applied to the rest of the section, several other potential organic shale targets are recognized. Each depth marker has a spacing of 100m.