



## Mudrock/Shale Chemostratigraphy with Handheld XRF

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Natural gas extraction from shale deposits has grown very rapidly in the last few years and now plays a major role in our current energy supply. Nineteen geographic locations all over the US are recognized sources of shale gas (Figure 1). Significant production takes place in Texas from the Barnett Shale play, in New Mexico from the Lewis Shale play, and in the northeast from the Marcellus Shale play.

These shale-bound gas reserves were already investigated as early as 1981, but could not be exploited until new techniques, such as hydraulic fracturing (“fracking”) and horizontal drilling, were developed and fielded in the late 90’s. The highly complex and variable deposits pose unique challenges from a technical point of view, as well as from the need to characterize the host rock since there is already a lack of definition as to what all constitutes a shale. Due to the unique nature of shale, each area or “basin” is different and requires a unique approach to pinpoint and extract the gas.

The following article will introduce you to an application of handheld XRF (HH XRF) developed by Dr. Harry Rowe. The application was designed to not only collect data to help with understanding



Figure 1: Natural gas extraction sites in North America.

and modeling of shale gas deposits, but also to help with exploration and production. Shale and mudstone rock are highly compacted, layered, fine-grained sediments with low permeability. Figure 2 shows split drill cores from the Marble Falls, Barnett<sup>1</sup> and Ellenberger Formation sequence. As one can see quite easily, there are not many visible differences from core box to core box. With an optical microscope, one can discern the layers better, but mineral identification remains difficult. We need to shorten the wavelength to see more detail. Once we employ “X-ray vision,” we are able to see how variable the layers are.

When we think about [X-rays and minerals](#), first and foremost we think of X-Ray Diffraction (XRD), a technique that provides us with qualitative and quantitative information about mineralogical content. Mineralogical XRD analysis is possible, but requires a good, reliable and reproducible refinement “recipe” for quantitative analysis, such as Bruker’s [TOPAS software](#). Unfortunately, there are no direct standards on how data are evaluated; everybody does it differently, which makes it very difficult to compare datasets. The biggest problem is the determination of the clay minerals and

minerals with variable chemistry, for example solid solutions such as feldspars. In addition, XRD requires a powder sample, which makes this technique quite labor intensive and not well suited for measuring a lot of samples in the field.

The solution is elemental concentrations, or “elemental geochemistry,” an X-ray fluorescence (XRF) technique that can be checked with XRD, but provides a cost-effective and non-destructive way to analyze large sets of core samples, and can be employed in the field. The bonus with elemental geochemistry is that some elements can provide additional information, which often proves useful: redox sensitive trace elements (RSTEs), such as molybdenum<sup>2</sup>, for example. An added bonus is that, not only can the model be checked with XRD, but elemental geochemistry can also tell us where to collect the limited XRD samples so as to optimize our efforts!

When we plot the elemental data as a function of sampling depth from the core (Figure 3), we can see the variability in elemental concentrations, and can compare the data with models that have been developed using data from similar deposits or prior drill sites of the same deposit.

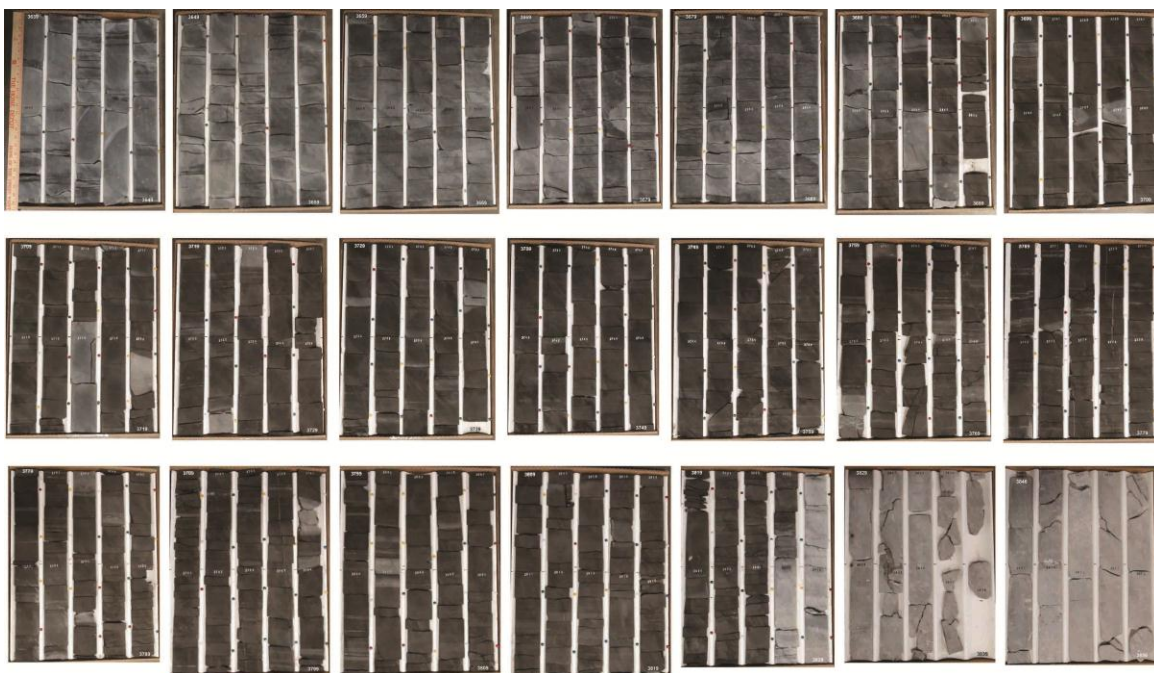


Figure 2: Shale and mudstone from the Marble Falls, Barnett and Ellenberger formations.



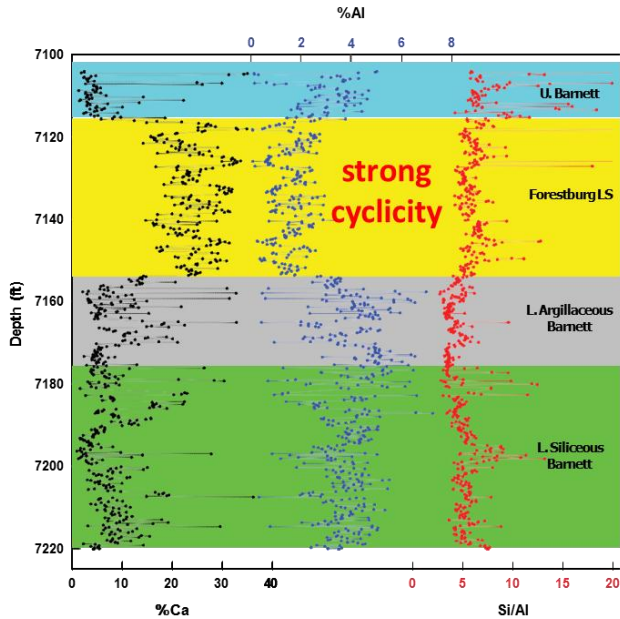


Figure 3: Elemental concentrations as a function of sampling depth from core samples.

The technique of chemostratigraphy relies upon recognizing changes in element concentrations through time and using those to model changes with respect to geological events, such as paleoclimate<sup>3</sup> and provenance<sup>4</sup>. The key is to enable “laboratory quality” data using HH XRF with a faster time to result, as well as the ability to scan cores from core repositories throughout the area and country.

Traditional “industrial” HH XRF is well suited for homogenous samples, such as alloys, and enables accurate grade identification on metals and decent chemistry, although it will not eliminate yet the need for mobile or laboratory chemistry data, e.g. by OES spark or XRF. The geo mode of HH XRF is generally based on the analysis of loose powders and greatly affected by the grain size and associated issues of sample homogeneity and mineralogical effects. Although it can trend the chemostratigraphy once it is “re standardized” to the basin, HH XRF will yield mostly only semi-quantitative data, which will be vastly different from unit to unit, as well as from setup to setup. Thus, the traditional HH XRF approach will not yield the desired publication-quality data required for studies<sup>5</sup>.

Dr. Harry Rowe developed extensive calibrations using his laboratory S4 PIONEER XRF instrument while at the University at Kentucky. He presented his application as part of Bruker’s XRF FOR YOU seminar series in Nashville, TN in June 2007 (Figure 4). With his first HH XRF unit, a TRACER, Rowe took full advantage of the provided software and applied the approach used for the S4 PIONEER to the TRACER<sup>6</sup>.

The largest obstacle was finding matrix-matched reference material. Dr. Rowe identified a set of shale samples and had the samples analyzed using XRF and ICP-MS for major and trace elemental composition at SGS Lakefield. This time, an S8 TIGER XRF and an Aurora mass spectrometer provided the data with calibrations based on decades of experience by the geochemists from SGS. Reference materials were selected in order to cover a wide range of materials in the shale.



Figure 4: Dr. Harry Rowe presenting at XRF FOR YOU Seminar in Nashville, TN In June 2007.

As shown in Figure 5, Rowe’s team defined a two-stage approach for the TRACER, making use of the unique capability of being able to control all settings of excitation like on a floor-standing or benchtop XRF system. For the detection of the major element suite, his team made use of the vacuum mode with an excitation voltage of 15 kV. For detection of minors and trace elements, a setting of 40 kV was selected. With the specially calculated multilayer

primary beam filter, the signal-to-noise ratio for the transition metals, as well as geologically important fingerprint metals, was improved to allow single-digit ppm detection limits.

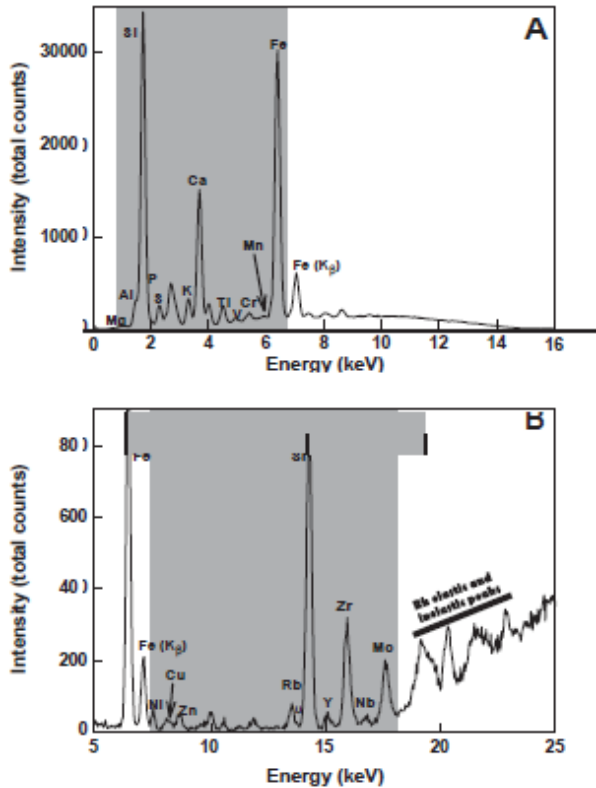


Figure 5: Two-stage core sample study approach with TRACER HH XRF: A) 15kV setting for major elements, and B) 40 kV setting for minor and trace elements.

In order to measure cores directly, the reference material has to be core-like in terms of density, which was achieved by using the pressed pellet approach (Figure 6) and employing no binder.

Measuring multiple spots on the same sample averaged out any mineralogical effects. Calibration was done using a modified Lucas Tooth and Pyne algorithm. The developed model was validated against reference methods (combustion, XRF and ICP)<sup>4</sup>.

By calibrating the TRACER hardware using these reference samples, identical setups were achieved and have been commercially available over the last

two years. The calibrated units are used extensively to measure all available core repositories to gather more data for modeling. Due to the inter-instrument consistency, various groups did pool data for HH XRF as well as for other different techniques to further model and understand the genesis of the various deposits. A number of publications at the GSA conference in 2013 was dedicated to the modeling of various basins, many based on data that included “mudrock” calibration-based stratigraphy.

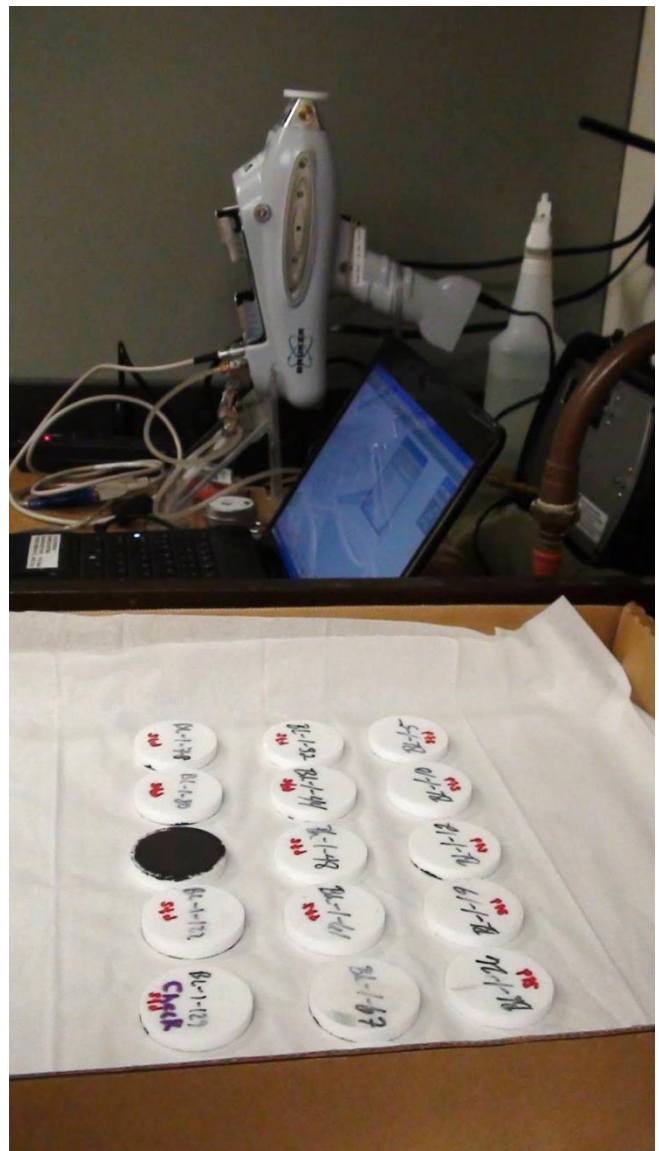


Figure 6: Pressed pellets of mudstone/shale shown in foreground, instrument in background.

The same approach is used by “loggers” on the drill rig to better recognize the turn-off point, where to go horizontal to get to the gas! Now we use the model and “predict” by chemistry. Although we can only indirectly predict the mineral content, we can use chemistry to direct the drill onsite using the drill cuttings.

Fast time to result allows for onsite decision making which will further advance the ability to exploit these unconventional and variable reservoirs. The more we know about where we are, the less chance of making mistakes that might endanger the water supply.

Why does this technique work? By employing matrix matched reference samples which have the same grain size as the rockface/drill core materials, we start with the most important reason. The second most important step is tough: not applying the application in point and shoot mode, but verifying each spectrum taken before getting concentrations:

- Check if it is really of the same matrix as the envisioned calibration.
- Check for elements which are not covered by the application.
- Check for intensity of element signals which exceed the respective calibration range, e.g. barium contamination from drill mud in non-cleaned drill cuttings.

Some of these steps can be automated, but nothing yet replaces the person behind the analyzer when it comes to quality data.

When employed as such, the HH XRF method of analyzing drill core materials is faster than traditional methods, and provides a comparable level of analytical certainty for most elements. More data points faster at less cost also enables shorter and more cost-effective drill campaigns.

The authors want to thank Harry Rowe and his many graduate and undergraduate students who validated the approach, as well as all the peer reviewers who insist on traceable analytical data.

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