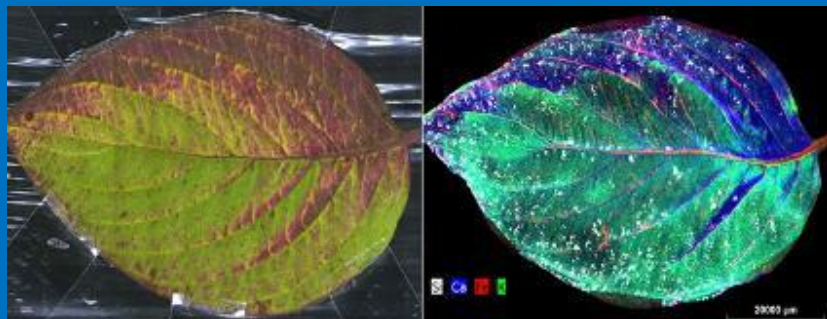




FIRST Newsletter October 2014, Issue 29

Strategy for Developing and Calibrating Shale and Mudstone Chemostratigraphies Using HH XRF, from Manual to Automated Core Logging

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Introduction

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. The highly complex and variable shale 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 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. Characterization can be performed with X-Ray Diffraction (XRD), a technique that provides qualitative and quantitative information about mineralogical content. Although mineralogical XRD analysis is possible, it requires a good, reliable and reproducible refinement “recipe” for quantitative analysis, such as Bruker’s TOPAS software. Datasets from different researchers or institutions are hard to compare because everybody uses different approaches and “recipe structures”. In addition, XRD requires a powder sample, which makes this technique quite labor intensive and not well suited for measuring many samples in the field or measuring samples from existing core repositories. Using Energy Dispersive X-Ray Fluorescence Spectrometry can produce elemental geochemistry

data, which in turn can be checked with XRD. It provides a cost-effective and non-destructive way to analyze large sets of core samples in the field or lab.

Strategy and Method

Shale and mudstone rock are highly compacted, layered, fine-grained sediments with low permeability. Figure 1 shows split drill cores from the Marble Falls, Barnett and Ellenberger Formation sequence. With a lack of available reference material, Rowe and Hughes (2012) selected a range

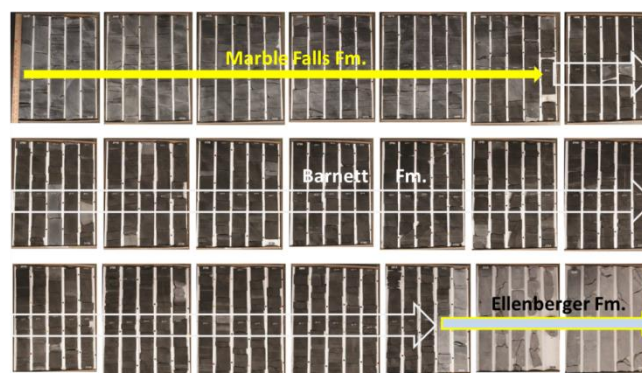


Figure 1: Core boxes of shale from Texas showing the lack of differentiation within the formations.

of shale samples, which he then had characterized fully as secondary standards that would cover the range of major and important trace elements found in the formations of interest. Rowe’s team defined a two-stage approach for the TRACER, making use of the unique ability to control all settings of excitation (similar to a floor-standing or a bench-top XRF system). For the detection of the major element suite, his team initially made use of the vacuum mode with an excitation voltage of 15 kV. For detection of minor and trace elements, a setting of

40 kV was selected. Using a 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. The filter was the standard yellow filter of the TRACER III or IV series.

In order to measure cores directly, the reference material must be core-like in terms of density, which was achieved by using the pressed pellet approach (Figure 2) 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 Price algorithm. The developed model was validated against reference method (combustion, XRF and ICP) as outlined in Rowe and Hughes (2012). Examples of the validation plots are shown in Figure 3.

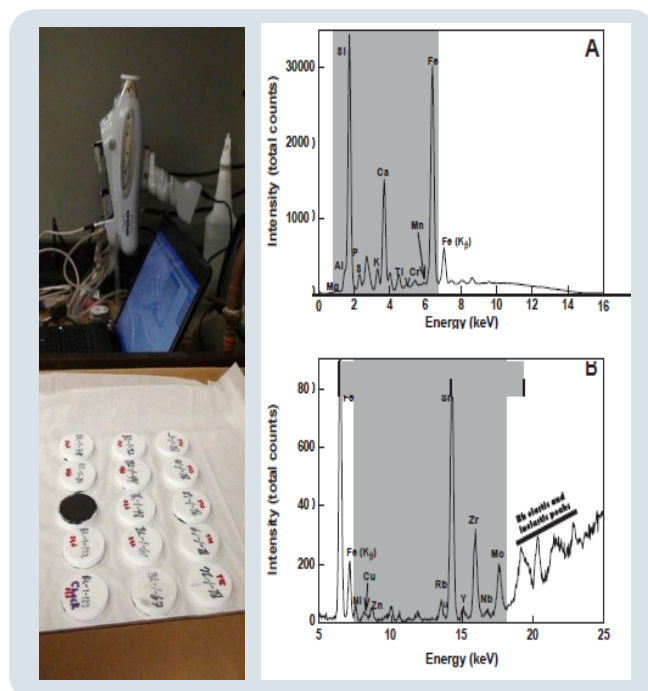


Figure 2: Pressed pellet of reference material (left) and spectral view of the two measurements modes (right).

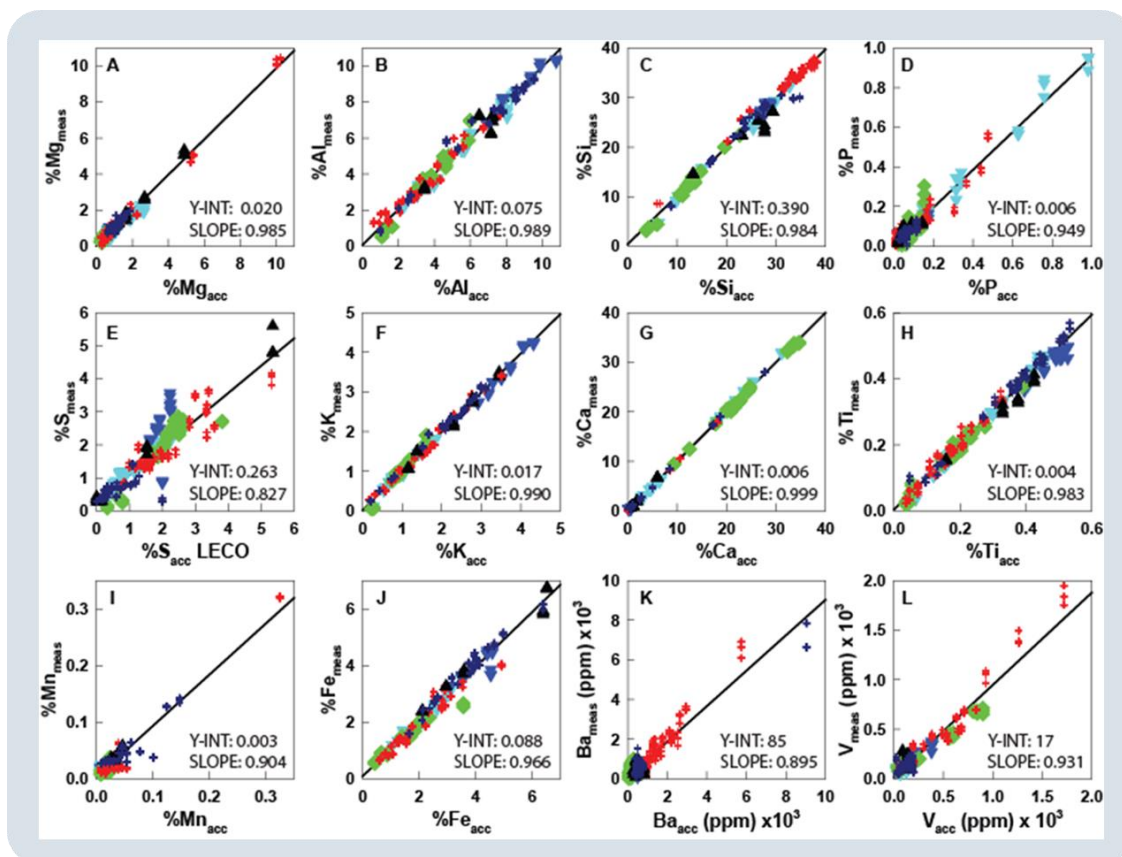


Figure 3: Validation of HH XRF vs. Reference (color coded by formation) from Rowe et al. 2012.

Application

The developed application was subsequently deployed on more TRACER units used to collect data from multiple core repositories containing material from both scientific and commercial drilling operations. To minimize cost and allow for fast data collection, the setup shown in Figure 4 was used. A more automated approach is available by integrating the TRACER into a third-party core scanner (DeWitt), which allows unattended operation and exact and repeatable positioning of the measurement spot.

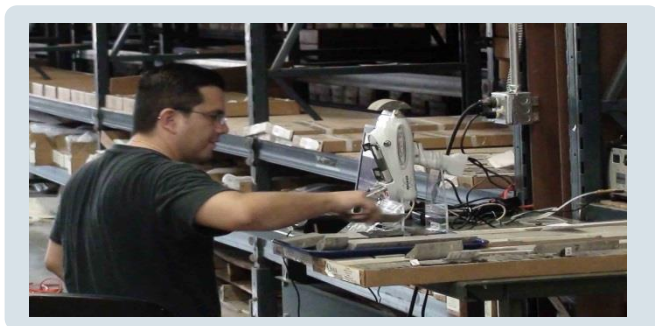


Figure 4: On the job scanning of core with a TRACER portable XRF (pXRF) unit.

The scanning of fresh core requires attention to detail since acquired data can readily be compromised when the core is not suitably clean or when brines re-emerge due to pressure relief of the material. The operator has to diligently screen the spectrum for surprises when the scanning is done manually as well ensure the instrument “nose” with its measurement spot is in contact with the sample. Calibration selection is done using the spectral view which is crucial because looking at numbers is more difficult and error prone.

As marked in Figure 5, Surprise #1 results from measuring a carbonate material interspersed with the mudrock. While indicative of the formation, it might also indicate that, in the measurement spot, XRF picked up a mix of mudrock and carbonate. The operator must then choose which calibration to use or select a different spot. Insufficiently cleaned core can be recognized by Ba contamination from the “mud” as in Surprise #2. Seeping brines are recognized with an increased signal of Cl which is overlaid on the scatter peak of the Rh X-ray tube line marked by Surprise #3.

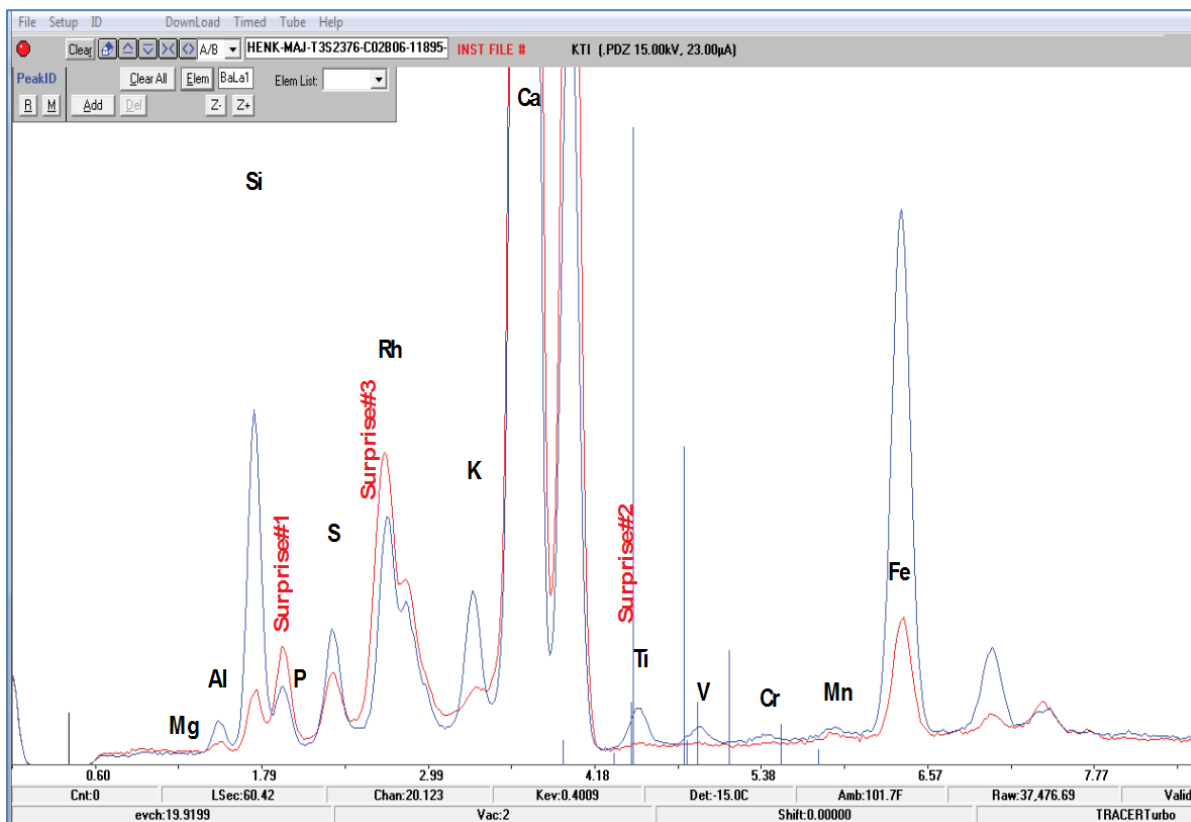


Figure 5: Low energy spectrum (15 kV) from core with “surprises”.

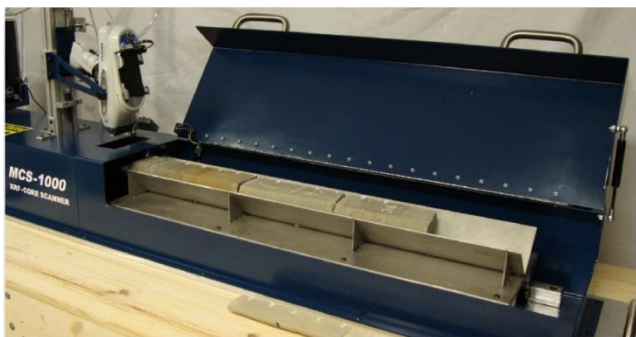


Figure 6: View of the MCS-1000 XRF Core Scanner, opened.

While this manual method works excellent in an academic environment thanks to the effort of graduate students a more automated approach though is required for industry. A newly developed core scanner accessory for the TRACER system by DeWitt (2014) enables this approach and also has a number of features setting it apart from other commercial core scanning systems.

The MCS-1000 combines the TRACER IV series system with a control system, helium purge, camera, barcode reader, exact indexed core movement and instrument positioning.

The TRACER IV is attached to a vertical arm and lowered onto the core surface ensuring contact. Once in contact the He purge is actuated displacing air in the nose cone of the TRACER and between it and the core surface. This allows the detection of all light elements from sodium (Na) onwards as well as higher sensitivity for Al and Si compared to air measurements. Positioning from the top down also

minimizes any contamination. No fancy and expensive laser sample height measurement is needed and the system is also tolerant to less than ideal flat cores such as fractured cores or cores with removed areas.

The measurement spot is documented with a high-resolution picture as well as the indexed position of the core. This is then converted to the absolute depth using the initially entered core information which also can be read via bar code. Based on the measurement strategy, the user can mark the desired measurement spots which are then recognized, or select a custom spacing of spots. During the data assessment, surprises as outlined earlier can be recognized and data consistency checks can be applied to ensure that the data are fit for purpose.

The MCS-1000 is sufficiently modular in designed to allow future expansion and has special control software, developed by DeWitt in conjunction with academic partners and Bruker, that includes the full functionality of the standard TRACER software package. Customers can have this software customized to interface with their proprietary systems for data exchange and to link obtained data to GIS and other systems.

Using the manually collected data or the data collected with an MCS core scanner it is possible to create quality chemostratigraphic plots of elemental abundance as a function of core sampling



Figure 7: Full view of the MCS-1000 Core Scanner with control system and PC.

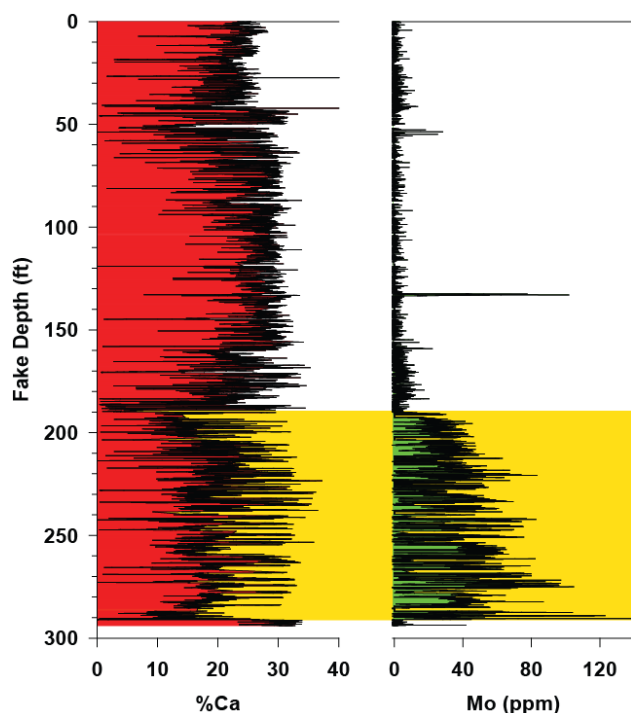


Figure 8: Fake "depth" vs elemental content of a data set comprising 8700 analyses from 33 boxes of core done over a 2-month period with the MCS-1000 (Rowe 2014).

depth (Figure 8 shows an example). Unlike other approaches that are limited to relative elemental abundance, the TRACER-based system enables the publication and use of quantitative data. Due to inter-instrument consistency, various groups pooled data for HH XRF, in addition to other techniques, to further model and understand the genesis of the various deposits. A number of publications at the 2013 GSA Conference were dedicated to modeling of various basins, many based on data that included "mudrock" calibration-based stratigraphy. This clearer understanding facilitates shale gas exploration. Of greater interest is shale gas *exploitation*, which uses a technique referred to as "fracking". Fracking relies on the accurate positioning of the horizontal turn-off in the "right" gas-yielding layer of the shale. Chemistry information is now used to pinpoint these turn-off locations, as well as the locations for the vertical "outlets" for the fracking liquid. The mineralogical and structural complexity of the shale "plays" – and the lack of macro or microscopic differentiation which otherwise could be used by drill-crew loggers to drive the drilling – requires the use of geochemical elemental concentrations at the drill

site. Quick 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.

Production Drill Operation

Most drilling operations aimed at production do not core, they only retrieve "cuttings". Even on these drill cuttings the TRACER system, with the appropriate calibration and care taken, can be used to obtain quality data.



Figure 9: Drill cuttings from an oil and gas drilling operation.

Conclusion

"Just point and shoot at cuttings," as incorrectly and simplistically portrayed by some HH XRF instrumentation companies, will not result in a reliable analysis. Quality analysis requires some preparation effort and instrumental traceability to a user calibration, in addition to well trained, conscientious operators and loggers. No amount of highly technical data processing can alleviate the quality of data collected under the "garbage in, garbage out" principle. Following standardized sample preparation methods and consistency checks enables quality data to be collected. Results from such data can then be correlated to the painstakingly acquired data on archived cores corresponding to production data and parameters. Therefore, with a relatively simple system onsite, one is able to tap into the "big data" cloud instead of "guesstimating" or even flying blind. This might result in more efficient control of the rig resulting in a more productive campaign. Cost-to-benefit data is highly classified and proprietary but it can readily be

said that a TRACER-controlled drill operation, in conjunction with a chemostratigraphic model of the area of interest, is hugely profitable. The onsite “mud logger” now has more quantitative data to share and report to the corporate geologist, thus substantially reducing costly mistakes and misconceptions.

For information on the chemostratigraphic approach and shale models of these unconventional resource “plays”, refer to the ever increasing number of publications or contact Dr. Harry Rowe’s working group at the Bureau of Economic Geology at the University of Texas in Austin.

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4. Seyfarth, A., Kaiser, B., Drake, L., Jan 2014, Bruker FIRST Newsletter: [Mudrock/Shale Chemostratigraphy with Handheld XRF](#).