Upstream Exploration & Production (E&P) with the Thermo Scientific Niton XL3t Series XRF Analyzer

Introduction

The worldwide exploration of shale gas is driving North American and European natural gas production. Shale gas, or tight gas, is a gas found in very low permeability rock that requires hydro fracturing; it must contain high amounts of silicon (Si). Recent studies have linked the abundance of redox sensitive trace metals – vanadium (V), chromium (Cr), uranium (U), thorium (Th), molybdenum (Mo), and rhenium (Re) – to strata that has increased organic paleo-productivity. This abundance serves as an indicator of gas potential in shale. Accurate stratigraphic correlations in these monotonous sequences of shale can be enhanced by chemostratigraphic techniques, employing the major, minor, and trace element abundances and ratios. X-ray fluorescence (XRF) is a technology that can be used to rapidly log the inorganic geochemistry of cuttings and cores in minutes in a centimeter (cm) scale.

Application

Thermo Scientific portable XRF analyzers provide users with the ability to analyze a variety of sample types common in the upstream E&P industry, including drill cuttings, cores, surface outcrops, and piston-cored sediments that are used in the exploration of hydrocarbons. Because the inorganic chemistry, and ultimately the mineral composition of the rocks, gives geologists important information about how the hydrocarbon is hosted within the rock and how it will be produced, the elemental analysis of those rocks is critical. Unlike metals mining, portable XRF cannot analyze hydrocarbon fluids. However, portable XRF can analyze bulk elemental chemistry of a reservoir that reflects properties that influence porosity (cement types), permeability (clays, cement type), fracturability (Si content), and productivity (Si, magnesium (Mg)), and trace metal content.

Recent internal studies show that the analyzer has the ability to log dolomite content of gas shale from drill cuttings, map the distribution of clays and cements in fault systems, and show subtle, but important, variations of trace metals in gas shale and piston cores. This indicates the usefulness of portable XRF in upstream E&P applications on a scale from cm to kilometers (km).

Figure 1. Rapid elemental analysis by handheld XRF and elemental ratio plots is a valuable tool in well logging and exploration.

Uses of Elemental Chemistry by Portable XRF in Upstream E&P

Specifically, the elemental chemistry provided by portable XRF analysis assists upstream E&P in a variety of ways:

- Identification of major rock-forming elements – light elements [Si, aluminum (Al), calcium (Ca), potassium (K), sodium (Na), and Mg), and iron (Fe)]
- Bulk chemistry gives sample mineralogy: silicates, aluminosilicates, carbonates, sulfides, (i.e., lower Si/Al indicates greater aluminosilicate content of rock)
- Element ratios can point the way to quantitative mineralogy: Si/Al, Ca/K, Fe/S, Si/Ca (i.e., Si/Al ratios between 5 and 22 indicate mixtures of clays, quartz, and feldspar)
- Geochemical information adds value to petrophysical logs (i.e., gamma "hot sands," etc.) that are run on every well that is drilled
- Bulk chemistry combined with mineral phase (structure) identification (fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), petrography, etc.) provides quantitative mineralogy
- Mineralogy determines hydrocarbon potential, reservoir quality, casing points, and fracture potential
- Ca/Mg ratios can provide a quantitative determination of the dolomite content of the carbonate rock

Method

The Thermo Scientific Niton XL3t Series handheld XRF analyzer with geometrically optimized large area drift detector (GOLDD™) technology is ideal for light element and trace metal analysis required for gas shale applications. Comparison of the Niton® XL3t Series XRF analyzer with independent laboratory results obtained by ICP-MS on 160 sedimentary rock samples and standards show typical correlations (R^2) > 0.90 and repeatability < 5% relative standard deviation (RSD) for most major, minor, and trace elements from Mg to U. Optimal results were obtained on pressed powder pellets with the use of an He purge system. Counting times were 30 seconds each on the low, main, and high energy filters (for analyzing Ti to U), and 60 seconds on the light filter setting (for analyzing Mg to S) for a total analysis time of 150 seconds. Studies of solid cores and cuttings provide results within 5 to 20% of this data quality.

Results

The correlation of XRF results with laboratory ICP results is shown in Figures 2-6 for Ca, K, Si, Al, and Mg. Element ratios can be accurately calculated using the analyzer's Pseudo-element feature, and used to determine the qualitative mineralogy of the rock.

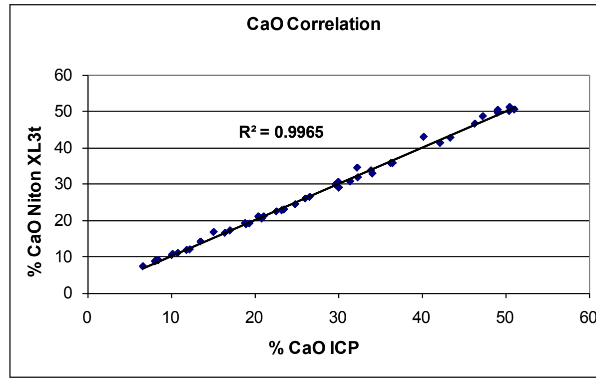

Figure 2. Correlation between CaO values measured by Niton XL3t Series analyzer and ICP-MS

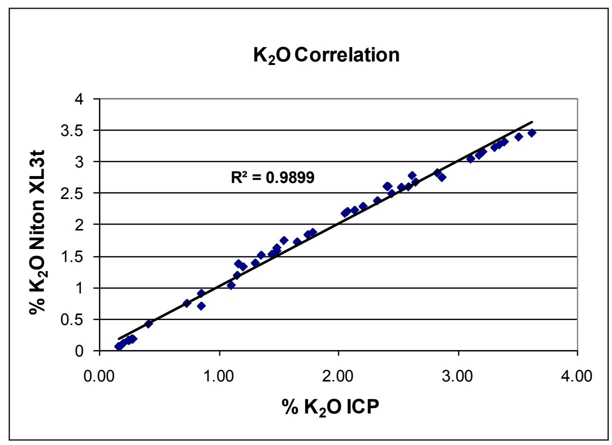

Figure 3. Correlation between K2O values measured by Niton XL3t Series analyzer and ICP-MS

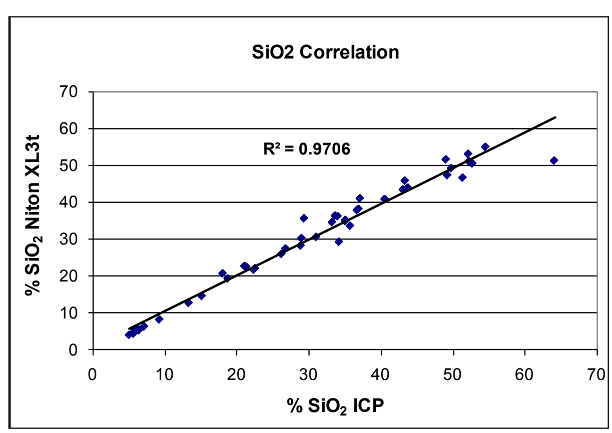

Figure 4. Correlation between SiO2 values measured by Niton XL3t Series analyzer and ICP-MS

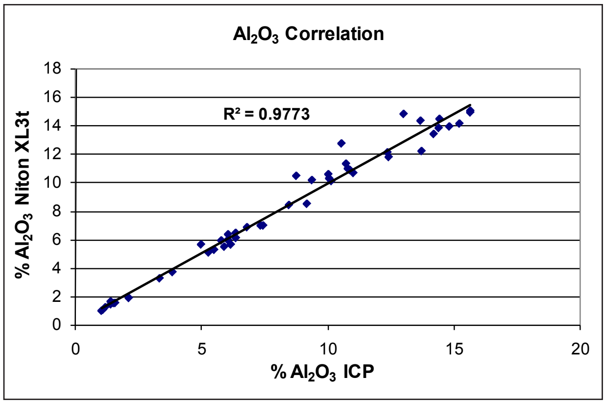

Figure 5. Correlation between Al2O3 values measured by Niton XL3t Series analyzer and ICP-MS

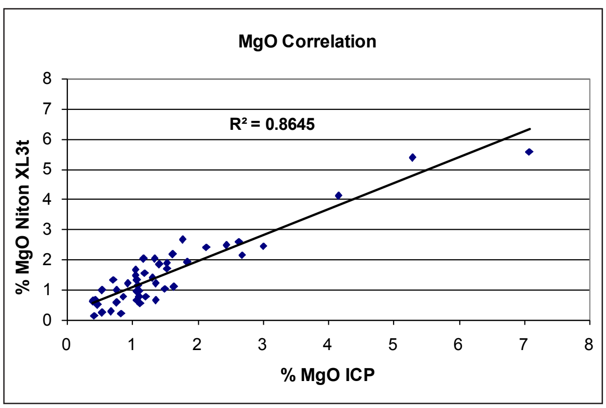

Figure 6. Correlation between MgO values measured by Niton XL3t Series analyzer and ICP-MS

Eagle Ford Case Study

The Eagle Ford Formation is a sequence of shale, siltstone, and limestone, which is an important source of rock and shale gas in Texas. Within the shale, there are very few visual indicators of stratigraphic position. An important difference between the Turonian/Cenomanian Age rocks is the separation of low from high total organic carbon (TOC) content sequences. TOC controls the amount of gas that can be generated within the shale. Redox sensitive trace elements (elements with multiple oxidation states, such as U, Mo, Cr, V, Ni, and Re) can pinpoint this boundary and can be related to the paleo-productivity of the rock.

The Mn, V, Cr, and Mo data presented in Figure 7 show a marked decrease in Mn and increase in V+Cr and Mo below the stage boundary. This correlates with increased TOC content of the cuttings. The sharp contrast in trace metals above and below the Turonian/Cenomanian boundary allows us to pinpoint the contact within feet. This case study clearly demonstrates that the Niton XL3t Series XRF analyzer can be used to accurately define stratigraphic intervals by chemical proxies. Bulk chemistry can be used to determine productive regions in gas shale. This is a major tool used in on-site well logging and as an aid to routine core analysis.

Montney Shale Case Study

The Montney Formation is a Triassic sequence of very fine-grained sandstone and siltstone in northeast British Columbia and western Alberta. Gas is hosted in the lower permeability (tight), finer-grained members of the formation (see Figure 8).

The formation is composed of quartz with variable amounts of clays and calcite cement; pyrite also can be present. Knowing the mineralogy of the various intervals encountered while drilling gives insight into

Figure 7. Gamma, total organic carbon (TOC), and elemental logs plotted as a function of depth in feet (6900' to 7300' total depth). Gamma intensity increases to the right; high values indicate the presence of radioactive elements trapped in shale. Note the minor changes in the gamma log throughout the depth interval. TOC and gamma data are from a previous Shell study. Mn, V, Cr, and Mo were analyzed with a 900 SDD on sand-sized drill cuttings in 20' composites. Samples were analyzed in mining mode (30 sec/filter, 60 sec/light filter) and soil mode (30 sec/filter). Data presented here is from soil mode data set. Note the marked decrease in Mn and increase in V+Cr and Mo below the boundary (green dashed line). This suggests anoxic conditions that preserved more organic material, which is consistent with the higher TOC values below the boundary.

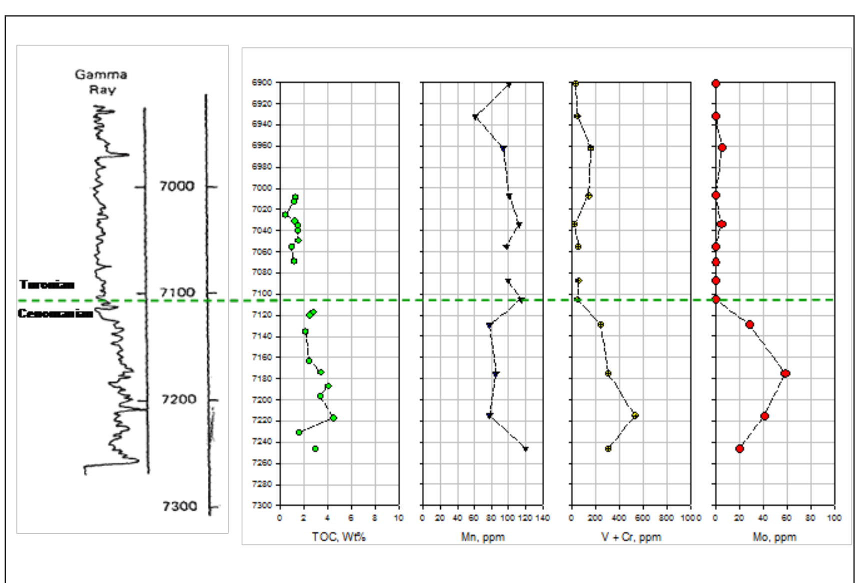

Figure 8. Gray, fine-grained sandstone and siltstone of the Montney Formation. Note the lack of visual distinguishing features.

the total porosity of the formation (see Figure 9). High Si/Al ratios tend to indicate lower total micro-porosity in shale gas reservoirs. From the total porosity, investigators can calculate an accurate estimate of the gas content of the shale.

Elemental ratios offer an advantage over elemental abundances because the accuracy of the analyses is not a factor when comparing data acquired under the same conditions (matrix type and sample prep). Relative shifts in elemental ratios can be used to quickly note increasing calcite, quartz, and clays in a formation for further follow up. Gas shales produce best in fracture prone intervals that are quartz- and calcite-rich. By identifying these intervals in the field, the geologist is better able to plan for the well's completion program. Rapid elemental analysis by handheld XRF and elemental ratio plots is a valuable tool in well logging and exploration.

Conclusion

Elemental analysis using the handheld Thermo Scientific Niton XL3t Series XRF analyzer imparts important information to exploration geologists. Elemental chemistry gives clues to the rock properties that could affect oil & gas accumulation like porosity (Si and Ca content), permeability (Si/Al, Mg, Ca and K as proxies for clays and dolomite), and the presence of undesirable minerals (clays, pyrite, and carbonate cement from Si/Al, Fe/S, and Mg/Ca ratios). This information can be included in the well logs, adding valuable information to aid in the interpretation of petrophysical data and offering greater value to exploration programs.

To discuss your particular applications and performance requirements, or to schedule an on-site demonstration, please contact your local Thermo Scientific portable XRF analyzer representative or contact us directly by email at niton@thermofisher.com, or visit our website at www.thermoscientific.com/niton.

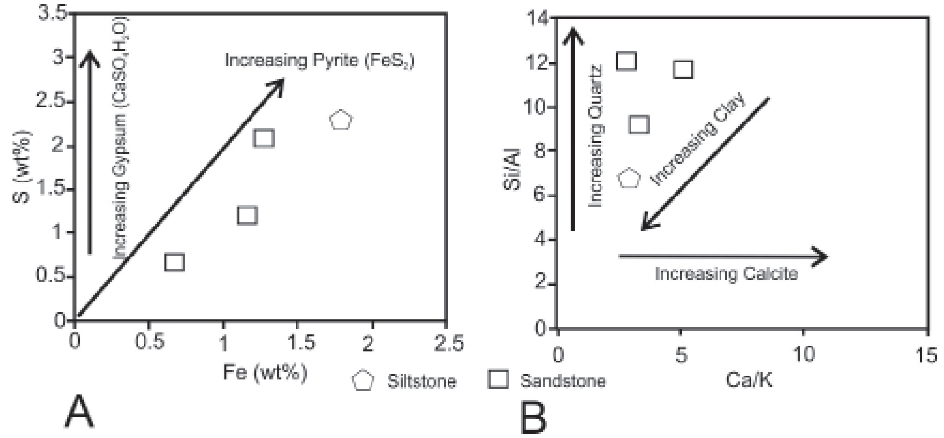

Figure 9. Major element plots help define relative mineralogy in the Montney using handheld XRF analysis. On the left: elemental abundance plot of Fe vs. S shows that the host mineral for the S is pyrite (FeS2) rather than gypsum (CaSO4H2O). On the right: elemental ratios of Si/Al is a basic indicator of the abundance of quartz (SiO2) vs. aluminosilicates, such as clays and feldspars. The combination of Si/Al and Ca/K ratios can show the relative amount of clay, quartz, and feldspar in the formation; for example, high Ca/K indicates the presence of calcite cement and high Si/Al shows increased quartz in the sandstone.

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