

## **Rapid Handheld X-ray Fluorescence (HHXRF) Analysis of Gas Shales**

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### **Abstract**

Handheld x-ray fluorescence is a powerful tool for detecting geochemical proxies indicating productive intervals in gas shale. Recent studies have linked the abundance of redox sensitive trace metals (e.g. V, Cr, U, Th, Mo, Re) to shale strata with increased organic paleo-productivity indicators and gas potential (Sageman et al., 2003; Ross and Bustin, 2009). Accurate stratigraphic correlations in these monotonous sequences of shale can be enhanced by chemostratigraphic techniques employing major, minor and trace element abundances and ratios. Handheld XRF provides a tool to rapidly log the inorganic geochemistry of cuttings and cores at the cm scale.

The Eagle Ford Formation is a sequence of shale, with minor siltstone and limestone that contains an important contact between the Turonian/Cenomanian age rocks, which separates low from high total organic carbon (TOC) shale sequences. Sand-sized drill cuttings in 20' composites were analyzed with a HHXRF instrument for a suite of 32 major, minor and trace elements. The results showed a marked decrease in Mn and increase in V+Cr and Mo below the stage boundary, correlating with increased TOC content of the cuttings. The change in V, Cr, and Mo reflects the variation in the oxygen content in the North American Sea way during Upper Cenomanian and Turonian time. The sharp contrast in trace metals above and below the Turonian/Cenomanian boundary allows us to pinpoint the contact within feet. This case study demonstrates that data from HHXRF analysis can be used to accurately define stratigraphic intervals by geochemical proxies. Bulk chemistry can be used to determine productive regions in gas shales – which can be an important tool used in onsite well logging and as an aid to routine core analysis.

### **Introduction**

The study of organic-rich shales has been driven by the need to understand source rock facies. The presence of large quantities of organic material in the water column allows for the effective sequestration of organo-metallc compounds in the sedimentary record, while depleting the trace metals present in the water column. Reduced sediments also allow for the precipitation and stabilization of metal sulfide compounds. Redox sensitive elements commonly found enriched in reduced, organic-rich shale include: V, Ni, Mn, Mo, Re, U, Zn and Cd.

### **Method**

Comparison of a Thermo Scientific Niton XL3t GOLDD HHXRF analyzer equipped with a silicon drift detector (SDD) with independent laboratory ICP-MS analytical results 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 (Fig. 1). Optimal results were obtained on pressed powder pellets with the use of a He purge system. Counting times were 30 seconds each on the low, main and high energy filters (for analyzing elements K to U), and 60 seconds on the light filter setting (Mg to S) for a total analysis time of 150 seconds.

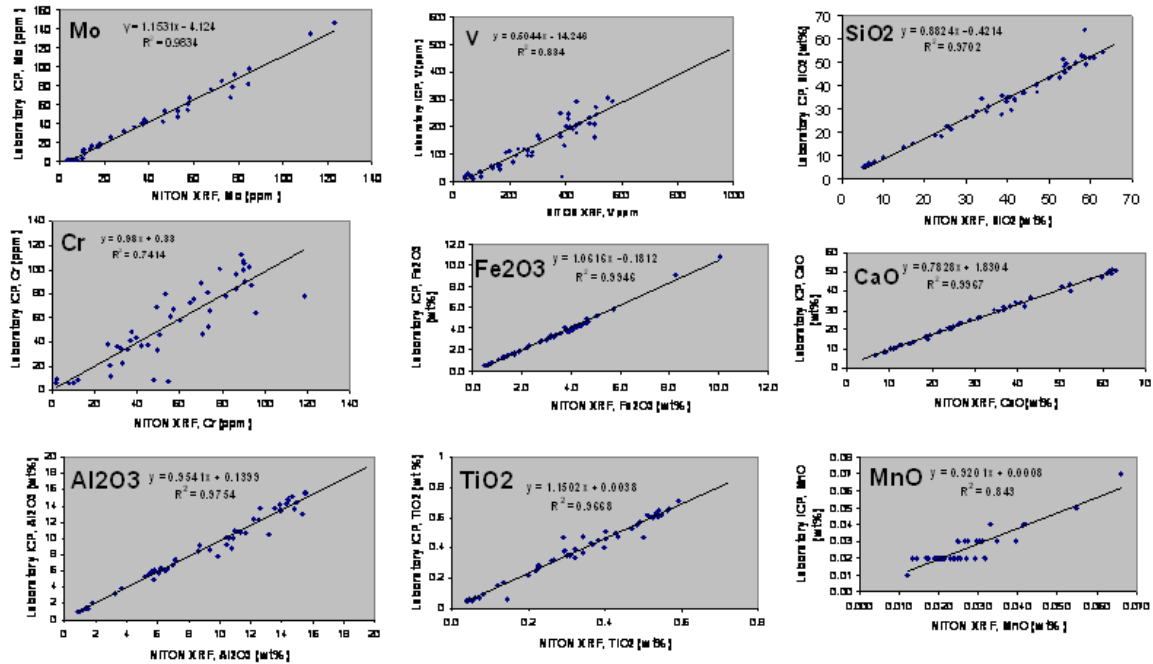


Figure 1. Comparison of Niton HHXRF data with samples run by ICP-MS in an independent laboratory show strong correlations with precision of < 5 % RSD for most elements from Mg to U.

### Eagle Ford Samples

Samples analyzed from Eagle Ford wells in Maverick, La Salle and Dimmit counties (Fig. 2) were sawn cores and sand-sized drill cuttings in 20' composites. The cores were analyzed in-situ and cuttings were analyzed directly without additional sample preparation. Counting times were 30 seconds each on the low, main and high filters and 60 seconds on the light filter. Data is presented as oxide wt%.



Figure 2. Eagle Ford study area in South Texas.

### Eagle Ford Trace Metal Geochemistry

Redox sensitive elements can help determine oxygen deficient conditions in bottom waters during shale deposition. Reduced conditions allow some elements such as V and Ni to be sequestered in organic matter. The presence of reduced sulfide can trap other metals in the sediments by forming metal sulfides (e.g. Mo, Cd and Zn) (Figs.3,4).

The plots in Figure 3 show the distinct grouping of high and low redox sensitive metals, V and Cr, by stratigraphic interval. The transition from anoxic to conditions of increased oxygen availability is marked by the decrease in V and Cr in the Upper Eagle Ford. The upper Eagle Ford has much lower TOC and therefore much less gas potential than the lower member. A map surface defined by the top of the lower Eagle Ford is a desirable exploration tool, as it would highlight the part of the formation most likely to host gas accumulations. Locating the top of the Upper Eagle Ford is difficult as it grades into the Austin Chalk. A map of the top upper Eagle Ford is likely to be located within the basal unit of the Austin Chalk and 10's to 100's of feet from the top lower Eagle Ford.

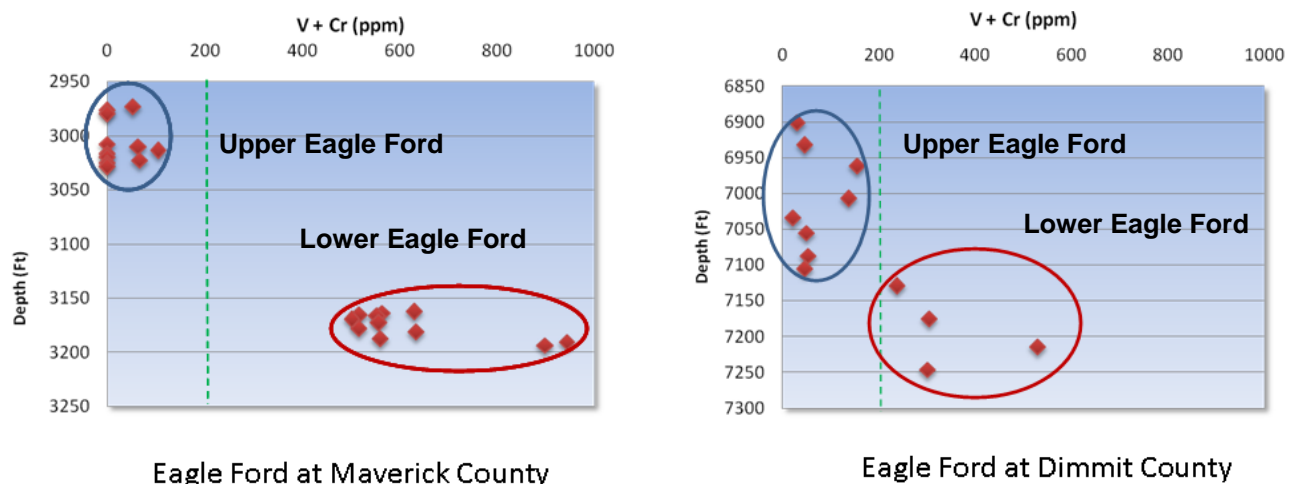


Figure 3. A sharp reduction in redox sensitive trace metals marks the contact between the upper and lower Eagle Ford.

### Eagle Ford Chemostratigraphy

Major and trace element geochemistry of rocks is a useful tool for stratigraphic correlation and provenance studies. Applied to the Eagle Ford Shale, variations in the mineralogy of the shale provide useful markers for the upper and lower Eagle Ford as well as defining the top of the formation and identifying the basal member of the Austin Chalk (Fig. 4).

Strong correlations between Ti and Al and Ti and Fe suggest a clay host (mixed illite-smectite) and/or a constant influx of detrital material to the sediments (Figs. 5, 6). The

sharp break in Ti and Al abundance at the contact between the shale and carbonate formations suggests that there is a very strong argument for clay as the Ti host (Fig. 4). The basal member of the Austin Chalk is marked by decreased Al and Si and increased Ca, although in core its appearance is very similar to the upper Eagle Ford. Decreased clay content in the Austin Chalk is also associated with lower Ti content.

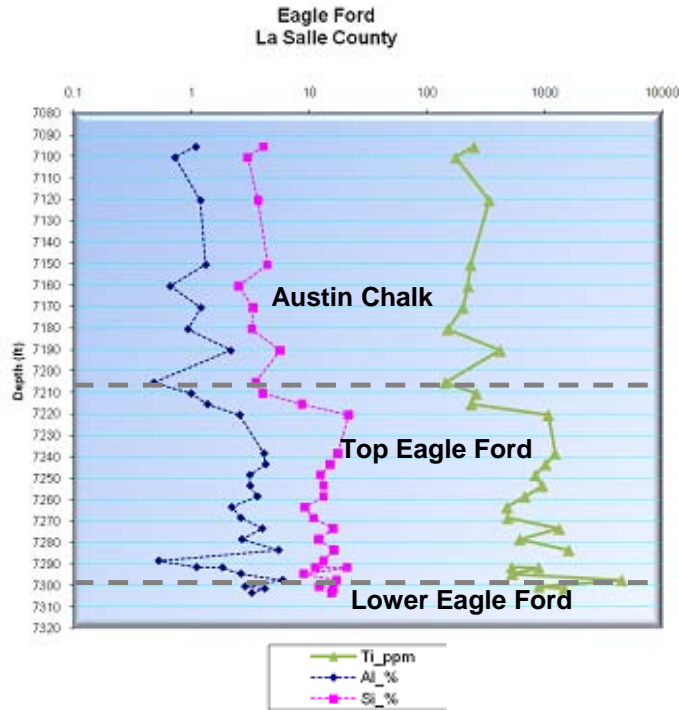


Figure 4. Strong correlation between Ti and Al suggest a clay host for Ti. A dramatic decrease in clay and silica content at the contact of the upper Eagle Ford marks the transition to the Austin Chalk. Top Eagle Ford picks by elemental geochemistry can vary from 10s to 100s of feet with picks made from logs.

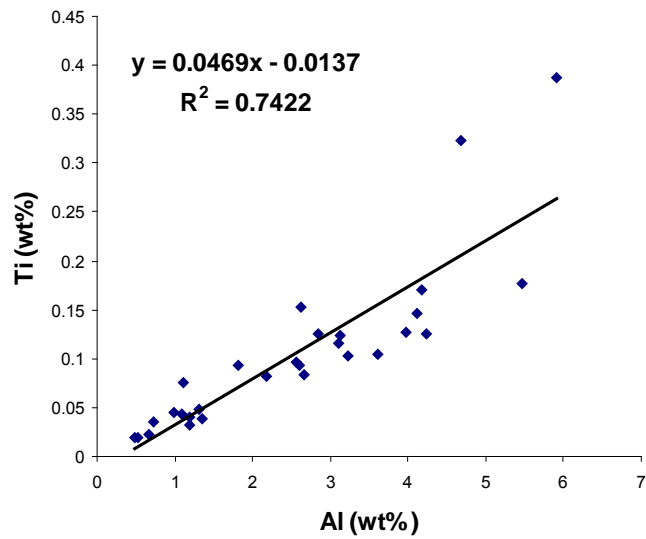


Figure 5. Correlation between Ti and Al from the Dimmit County well.

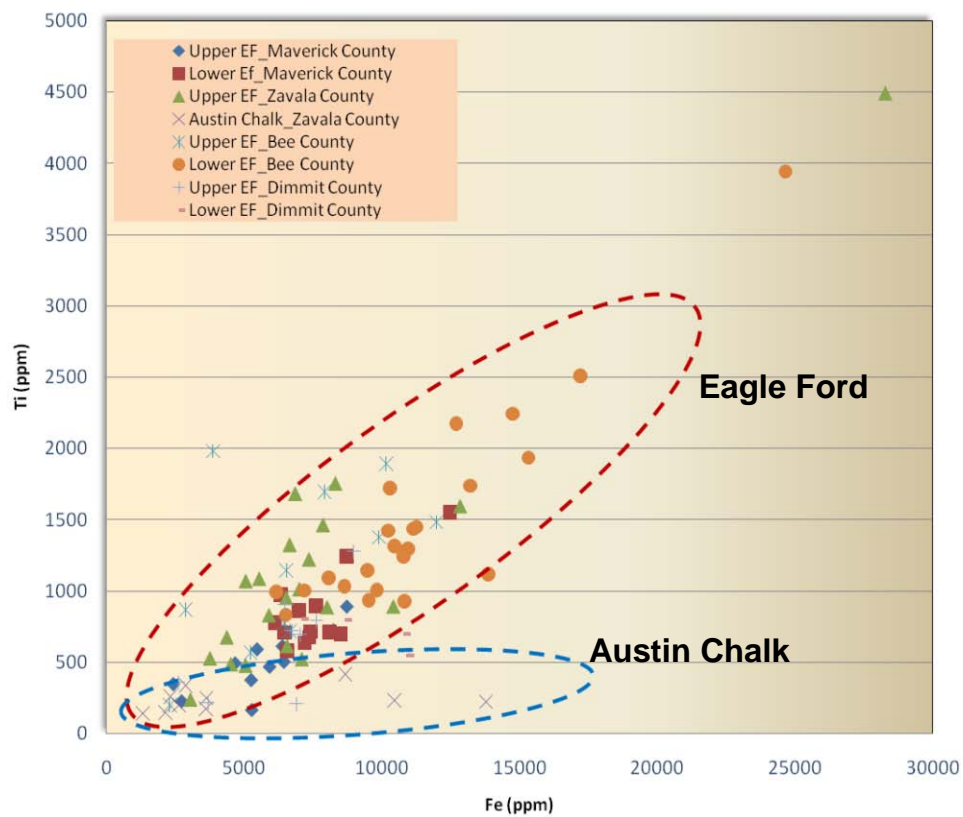


Figure 6. A plot of Fe vs. Ti shows both a high and low Ti trend depending on lithology. The trend of increasing Ti with Fe in the Eagle Ford shale suggests a mixed clay host for both elements or a steady influx of detritus during deposition. The correlation of Ti with

Al (Fig. 6) would make clays the likely host mineral. The much lower Ti content of the Austin Chalk indicates limited clay content in the carbonate.

A plot of Ti vs. Fe displays two distinct trends associated with the Eagle Ford and Austin Chalk formations (Fig. 6). The covariance between Ti and Fe suggest that these elements are hosted in the same mineral, most likely mixed illite-smectite. The range of Ti and Fe in the Eagle Ford reflects variable clay content based on position within the formation, upper and lower Eagle Ford, and geographic position, reflecting distribution of facies.

### **Conclusions**

The distribution of redox sensitive metals and major and trace element geochemistry can provide useful tools in the evaluation of gas shales. Obtaining dense data sets of elemental chemistry on cores and cuttings is crucial in these studies. Hand held x-ray fluorescence can provide large quantities of data in a short amount of time without extensive sample preparation or lab expense. The portable analyzer is suitable for use in the core room, field or logging trailer.

### **References**

- Ross, D.J.K. and Bustin, R.M., 2009, Investigating the use of sedimentary geochemical proxies for paleoenvironment interpretation of thermally mature organic-rich strata: Examples from the Devonian-Mississippian shales, Western Canadian Sedimentary Basin, *Chemical Geology*, v. 260, p. 1-19.
- Sageman, B.B., Murphy, A.E., Werne, J.P., Ver Straeten, C.A., Hollander, D.J. and Lyons, T.W., 2003, A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle-Upper Devonian, Appalachian basin, *Chemical Geology*, v. 195, p. 229-273.