[PS]Strategy for Developing and Calibrating Shale and Mudstone Chemostratigraphies Using Hand-Held X-ray Fluorescence Units*

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Abstract

Chemostratigraphy involves the identification of shifts in geochemistry within a section of strata, which can be used as a correlation tool or to help make inferences about the paleodepositional environment of a unit. Traditionally methods such as wavelength-dispersive x-ray fluorescence (WDXRF) or inductively coupled plasma mass spectrometry (ICP-MS) have been used to obtain geochemical data; however, energy dispersive x-ray fluorescence (ED-XRF) provides a more efficient means of data collection by using portable equipment that allows the investigator to take non destructive direct measurements.

While undertaking ED-XRF analysis of mudstones, it has been determined that calibrated results from the handheld ED-XRF effectively define chemostratigraphic changes in real time. When compared with WD-XRF systems, the much lower cost and enhanced portability of the typical EDXRF systems provide an exceptional tool for linking down core geochemical changes to stratigraphic, sedimentological, and paleontological observations. Furthermore, with a working calibration, quantitative results can be used to assess the dominant mineral phases within an interval. Results from several cores are evaluated in the study, including: the Devonian-Mississippian Woodford and Barnett shales; Pennsylvanian Smithwick shale; Cretaceous Eagle Ford shale. Pressed pellet standards from the Smithwick, Barnett, Woodford, and Eagle Ford, along with various international standards were used to create a matrix-specific calibration for organic-rich and organic-poor mudstones. The calibration is used to quantify major and trace elements for all cores.

STRATEGY FOR DEVELOPING AND CALIBRATING SHALE AND MUDSTONE CHEMOSTRATIGRAPHIES USING HANDHELD X-RAY FLUORESCENCE UNITS

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EXPLORATION AND PRODUCTION OF SHALE GAS RESOURCES
POSTER BOOTH NUMBER: 18D

ABSTRACT

Chemostratigraphy involves the identification of shifts in geochemistry within a section of strata, which can be used as a correlation tool or to help make inferences about the paleodepositional environment of a unit. Traditionally methods such as wavelength-dispersive x-ray fluorescence (WD-XRF) or inductively coupled plasma mass spectrometry (ICP-MS) have been used to obtain geochemical data; however, energy dispersive x-ray fluorescence (ED-XRF) provides a more efficient means of data collection by using portable equipment that allows the investigator to take non-destructive, direct measurements.

While undertaking ED-XRF analysis of mudstones, it has been determined that calibrated results from the handheld ED-XRF effectively define chemostratigraphic changes in *real time*. When compared with WD-XRF systems, the much lower cost and enhanced portability of the typical ED-XRF systems provide an exceptional tool for linking down-core geochemical changes to stratigraphic, sedimentological, and paleontological observations. Furthermore, with a working calibration, quantitative results can be used to assess the dominant mineral phases within an interval.

Results from several cores are evaluated in the study, including: the Devonian-Mississippian Woodford and Barnett shales; Pennsylvanian Smithwick shale; Cretaceous Eagle Ford shale. Pressed pellet standards from the Smithwick, Barnett, Woodford, and Eagle Ford, along with various international standards were used to create a matrix-specific calibration for organic-rich and organic-poor mudstones. The calibration is used to quantify major and trace elements for all cores.

GOALS

GOAL#1 OF THE PRESENT WORK IS TO OUTLINE THE STEPS REQUIRED TO DEVELOP QUANTITATIVE CHEMOSTRATIGRAPHIES FROM DRILL CORE MATERIALS USING A HANDHELD XRF.

GOAL#2 IS TO DEMONSTRATE HOW ROBUST HANDHELD XRF-GENERATED RESULTS ARE WHEN COMPARED WITH RESULTS GENERATED USING MORE TRADITIONAL INSTRUMENTATION.

GOAL #3 IS TO PRESENT AND INTERPRET TYPICAL CHEMOSTRATIGRAPHIC RECORDS FROM SEVERAL DRILL CORES IN ORDER TO SHOW THEIR UTILITY FOR BOTH INDUSTRY AND ACADEMIC NEEDS.

ISSUE #1: OFTENTIMES SHALE AND MUDSTONE SEQUENCES VISUALLY APPEAR STRATIGRAPHICALLY HOMOGENEOUS (FIGURE 1).

THIS MAKES IT DIFFICULT TO IMMEDIATELY IDENTIFY:
- WHICH PART OF THE SECTION IS BEING OBSERVED
- WHICH FINE-GRAINED UNIT/FORMATION IS BEING STUDIED (IN A LARGER SEQUENCE WITH MULTIPLE MUDROCK UNITS)

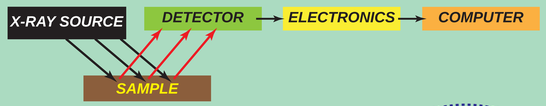
ONE SOLUTION IS TO DEVELOP A CHEMOSTRATIGRAPHIC RECORD FROM CORE MATERIALS THAT WILL ASSIST IN FUTURE STUDIES OF HOMOGENOUS STRATA.

THIS IS MOST EFFICIENTLY (RAPIDLY) ACCOMPLISHED USING A HANDHELD X-RAY FLUORESCENCE UNIT (FIGURE 2), WHICH ARE MANUFACTURED BY SEVERAL COMPANIES.

REVIEW: X-RAY FLUORESCENCE

WHAT ARE WE MEASURING?
WE ARE MEASURING THE ENERGY SPECTRUM FROM SECONDARY X-RAYS THAT HAVE BEEN GENERATED BY A HIGH-ENERGY X-RAY SOURCE BOMBARDING A ROCK SAMPLE.

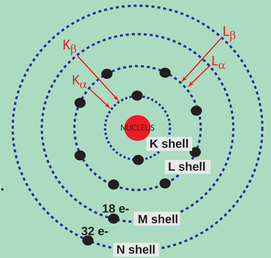
FIGURE 3: Schematic of ED-XRF.



THE X-RAY SOURCE (RHODIUM IN THIS CASE) EMITS HIGH-ENERGY X-RAYS THAT KNOCK INNER-SHELL ELECTRONS OUT OF THEIR SHELLS.

AN OUTER-SHELL ELECTRON FALLS INTO THE INNER SHELL TO FILL THE VOID, GIVING OFF A X-RAY WITH A CHARACTERISTIC ENERGY.

THIS X-RAY IS DETECTED AND COUNTED (FIGURES 4&5).



The energy spectrum generated is *characteristic* of the elements and their concentrations within the sample being analyzed.

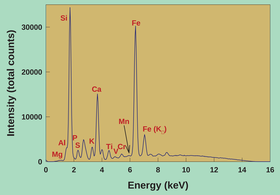


FIGURE 4: Low-energy dispersive x-ray spectrum of a typical low-calcium mudrock from the Barnett Formation, Mississippian, Fort Worth Basin, TX.

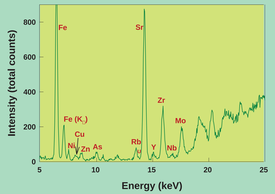


FIGURE 5: High-energy dispersive x-ray spectrum of a typical mudrock from the Eagle Ford Formation, Cretaceous, South Texas.

ISSUE #2: HOW DO WE CALIBRATE THE ENERGY SPECTRA FROM CORE SAMPLES IN ORDER TO QUANTITFY DOWN-CORE CHANGES IN GEOCHEMISTRY?

PROBLEM#1: VERY FEW SHALE/MUDROCK STANDARDS

PROBLEM #2: NARROW RANGE OF ELEMENTAL CONCENTRATIONS IN STANDARDS

PROBLEM #3: HOW IMPORTANT ARE THE MATRIX DIFFERENCES BETWEEN STANDARDS AND SAMPLE "UNKNOWNS"?

SOLUTIONS

1) DEVELOP A SERIES OF "REFERENCE MATERIALS" THAT SUPPLEMENT THE FEW INTERNATIONAL STANDARDS (e.g., SDO-1, SCo-1, SGR-1, SARM-41)

2) REFERENCE MATERIALS SHOULD BE DEVELOPED FROM MULTIPLE SHALE/MUDROCK UNITS THAT EXEMPLIFY A WIDE RANGE IN COMPOSITIONS OF MAJOR ELEMENTS (e.g., Si, Ca, Fe), AND TRACE ELEMENTS (V, Cr, Ni, Cu, Zn, etc.).

THE SUITE OF REFERENCE MATERIALS USED TO CALIBRATE THE CHEMOSTRATIGRAPHIC RECORDS PRESENTED HERE WERE CHOSEN FROM A MULTITUDE OF SHALE/MUDROCK UNITS SPANNING DEVONIAN THROUGH CRETACEOUS AGES, VARIABLE MINERALOGICAL AND ORGANIC CARBON CONTENTS, AND PALEODEPOSITIONAL CONDITIONS.

REFERENCE MATERIALS WERE CHOSEN TO MAXIMIZE THE FULL RANGE IN ELEMENTAL CONCENTRATIONS WITHIN THEIR RESPECTIVE UNIT/FORMATION.

"ACCEPTED" VALUES FOR SUPPLEMENTAL REFERENCE MATERIALS WERE DETERMINED BY SAMPLE ANALYSIS VIA FUSED-PELLET WD-XRF (FOR MAJORS), AND VIA FUSED-BEAD/ACID DISSOLUTION (FOR TRACE ELEMENTS). SGS MINERALS (TORONTO, CANADA) ANALYZED REFERENCE MATERIALS FOR THE PRESENT STUDY.

SUITE OF REFERENCE MATERIALS UTILIZED FOR CALIBRATION OF LOW-ENERGY (MAJOR ELEMENTS) AND HIGH-ENERGY (TRACE ELEMENTS)

- Ohio Shale, Devonian-Mississippian, Appalachian Basin, KY (n = 7)
- Smithwick Fm., Pennsylvanian, Fort Worth Basin, TX (n=20)
- International Reference Materials (n=5)
- Woodford Fm., Devonian-Mississippian, Permian Basin, TX (n=28)
- Eagle Ford Fm., Cretaceous, Gulf Coast, TX (n=15)
- Barnett Fm., Mississippian, Fort Work Basin, TX (n=16)

INSTRUMENTATION AND SETTINGS

INSTRUMENT: BRUKER TRACER III/V ED-XRF

LOW-ENERGY SETTINGS: 15 kV, 42 μA, NO FILTER

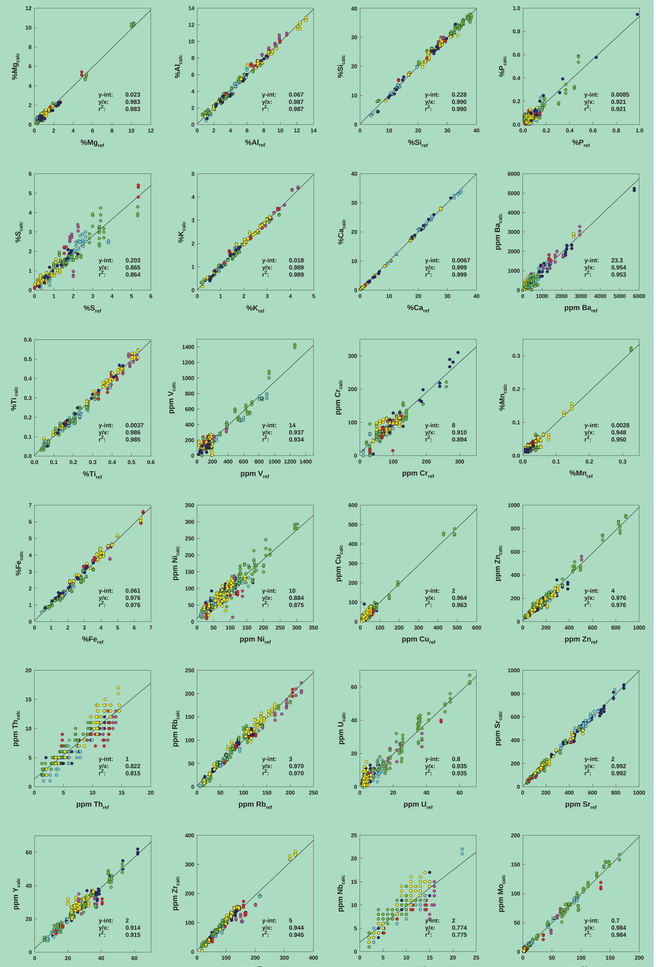
HIGH-ENERGY SETTINGS: 40 kV, 28 μA, Cu-Ti-Al FILTER

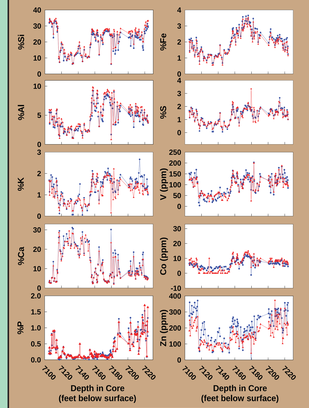
ADDITIONAL ISSUES:

PROBLEM#1: NEED FOR REFINEMENT (IF POSSIBLE) FOR %P

PROBLEM #2: NEED FOR REFINEMENT OF %S (REQUIRES USE OF ADDITIONAL FILTER, WHICH MEANS AN ADDITIONAL ANALYSIS, SEPARATE FROM MAJORS AND TRACE)

PROBLEM #3: NEED TO QUANTIFY ACCEPTABLE ENVELOPE OF MATRIX HETEROGENEITY (THIS MAY BE USER-DEFINED, AND PROCESS-SPECIFIC, BASED UPON THE ULTIMATE NEEDS OF THE STUDY)





ED-XRF COMPARED TO WD-XRF

Wavelength-dispersive x-ray fluorescence (WD-XRF) has been widely used for geochemical analysis; however, it requires sample preparation and analysis downtime that the energy-dispersive x-ray fluorescence (ED-XRF) does not. Both techniques operate based on unique properties associated with each element from electron shifts caused by x-ray bombardment. The light emitted from an electron transition is measured on the WD-XRF, whereas the energy emitted is detected in ED-XRF.

Wavelengths disperse easier than energy and display less background interference, which can make the peak data easier to resolve, but absorption coefficients will factor into the calibration for either method. The difference in resolution between WD-XRF and ED-XRF is not very significant with major elements due to higher concentrations. However, detection limits associated with ED-XRF for trace elements are typically higher than WD-XRF and affect the reliability of trace element data. This means that certain trace elements may be obtained in some cores with reasonable certainty and not in others using ED-XRF, but with a low enough concentration neither method will be effective. Overall, the ED-XRF provides very comparable results to that of the traditional WD-XRF and offers greater efficiency.

It is also important to note that the calibrations for the ED-XRF results and WD-XRF results in the figures to the left are completely different (different standards used in each), but still have similar results.

STRATEGY FOR DEVELOPMENT OF TECHNIQUE (*IF JUST STARTING*)

SCAN TYPICAL CORE MATERIALS

ANALYZE AND COMPARE ALL RAW SPECTRA, THEN PICK OUT SAMPLES THAT REFLECT THE FULL RANGE OF ELEMENTAL CONCENTRATIONS

SUB-SAMPLE THE CORE MATERIALS, PULVERIZE THEM, AND ANALYZE THEM USING FUSED-DISC WD-XRF AND ICP-MS (AT SEVERAL LABS, IF POSSIBLE)

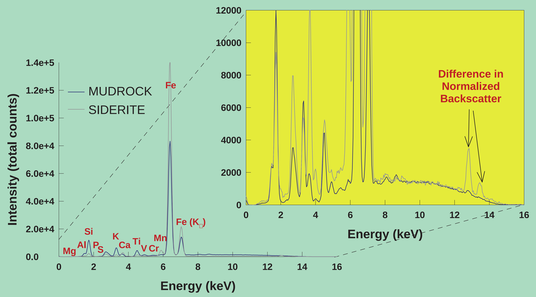
USE RESULTS AND SPECTRA OF PRESSED PELLETS TO CREATE CALIBRATION DATASET

ANALYZE CHECK SAMPLES AND UNKNOWNS, THEN RUN SPECTRA THROUGH CALIBRATION. COMPARE X-RAY BACKSCATTER SPECTRA TO EVALUATE APPLICABILITY OF CALIBRATION TO UNKNOWNS

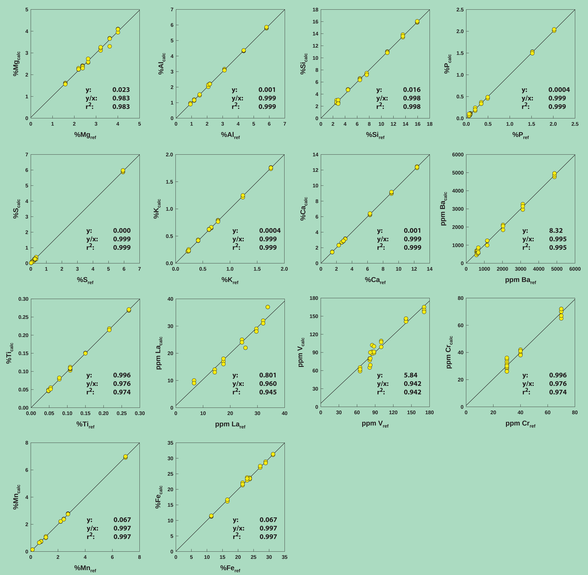
EXPECT A "MATRIX CURVEBALL"

MATRIX CURVEBALL: SIDERITE!!

The Smithwick Formation (Pennsylvanian, central Texas) has two dominant matrices: Mudrock *and* siderite (Fe-carbonate)

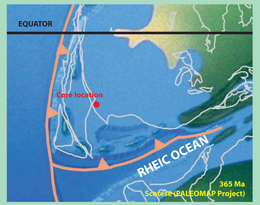


A calibration was developed to quantify the siderites and siderite-rich mudrocks:



WOODFORD FORMATION CHEMOSTRATIGRAPHY
DEVONIAN-MISSISSIPPIAN, PERMIAN BASIN, WEST TEXAS

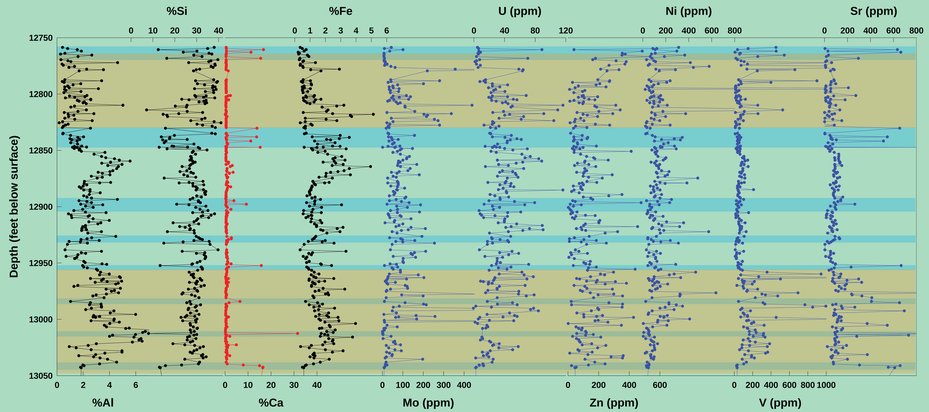
(CORE LOCATION IS PROPRIETARY INFORMATION)



CHANGES IN CHEMOSTRATIGRAPHY ARE NOT DOMINATED BY DILUTION BY ANY ONE COMPONENT (SEE EAGLE FORD, BELOW).

WOODFORD IS RELATIVELY LOW IN CALCIUM, SO THAT PEAKS IN Ca (AND STRONTIUM) MAY HELP DEFINE THE LOCATION WITHIN THE SECTION.

WOODFORD IS CHARACTERIZED BY TWO ZONES OF HIGH REDOX-SENSITIVE TRACE ELEMENT CONCENTRATIONS, SEPARATED BY ZONE OF RELATIVELY LOW ENRICHMENT.

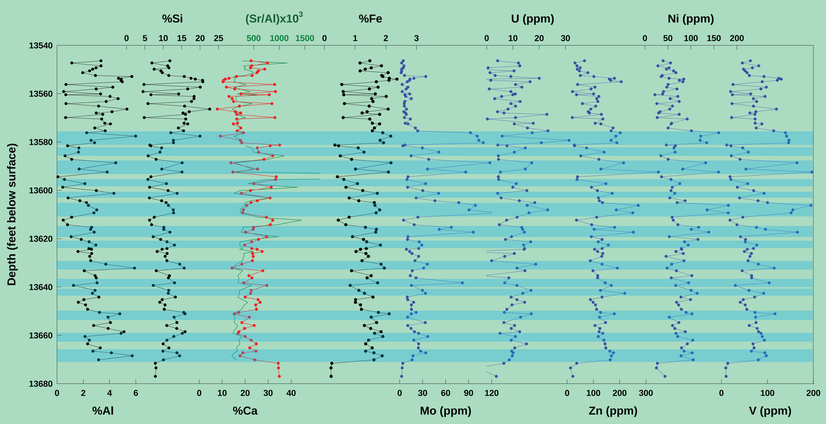


EAGLE FORD FORMATION CHEMOSTRATIGRAPHY
CRETACEOUS, GULF COAST, SOUTH TEXAS

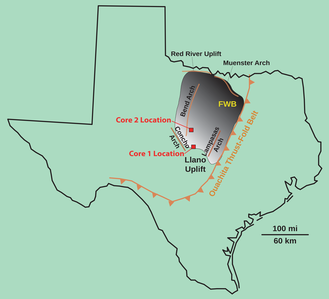
(CORE LOCATION IS PROPRIETARY INFORMATION)

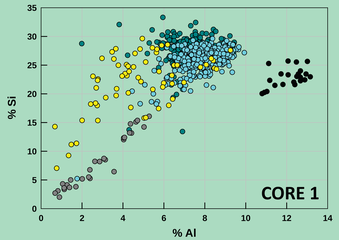
CHANGES IN CHEMOSTRATIGRAPHY ARE DOMINATED BY CALCITE DILUTION DILUTION (SEE RED GRAPH, RIGHT). MOST PEAKS IN Ca ALSO DEFINED BY PEAKS IN Sr/Al, INDICATING THAT NON-CLAY SUPORTED Sr IS SUPPORTED WITHIN THE CALCITE PHASE.

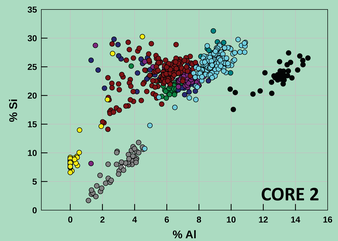
CYCLICITY IN REDOX-SENSITIVE TRACE ELEMENTS (ESPECIALLY Mo, Ni, AND V) HELP DEFINE LOCATION WITHIN THE SECTION. CYCLICITY IS STILL LARGELY DEFINED BY CHANGES IN %Ca.



SMITHWICK FORMATION CHEMOSTRATIGRAPHY
PENNSYLVANIAN, FORT WORTH BASIN, CENTRAL TEXAS
(CORE LOCATION IS PROPRIETARY INFORMATION)

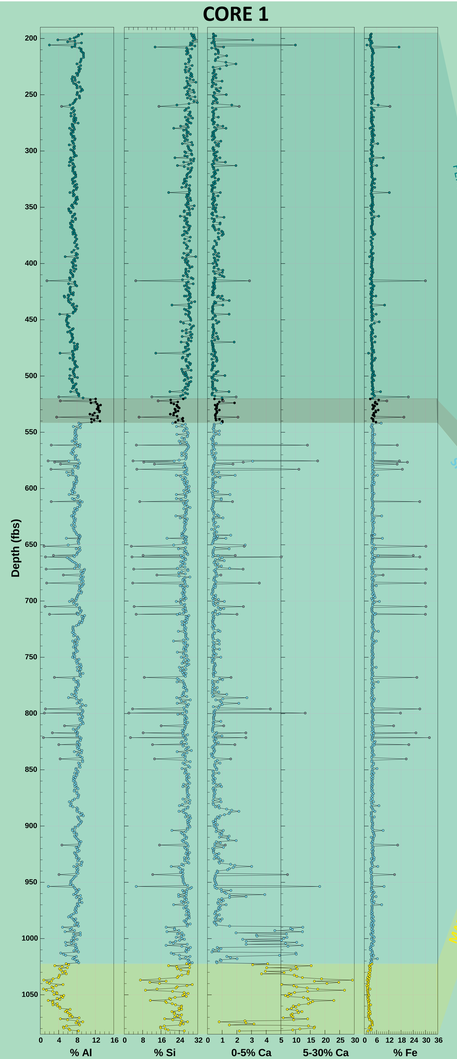


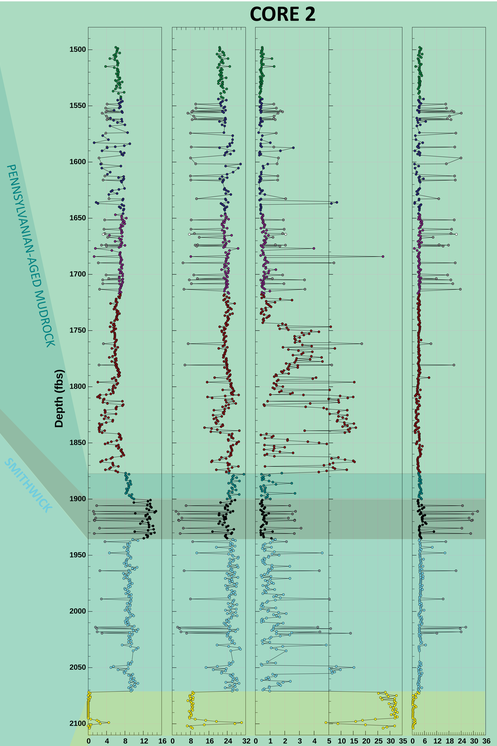




KEY FOR ALL GRAPHS:

●	GREEN:	DARK GREY TO GREY MUDROCK, GREEN TINT WITH RED-STAIN
●	BLUE:	INTERBEDDED MUDROCK & SANDSTONE; SILTY AND ORGANIC LAYERS
●	PURPLE:	DARK GREY (OR-STAIN) MUDROCK WITH INTERMITTENT THIN SAND BEDS
●	RED:	GREY (CA-DILUTED) MUDROCK, SOME ALTERNATING LAMINATIONS
●	DARK CYAN:	DARK GREY TO BLACK MUDROCK; SHELL MATERIAL
●	BLACK:	BROWN AL-RICH MUDROCK; FRACTURES WITH SLICKENSIDES
●	LIGHT CYAN:	DARK GREY TO BLACK MUDROCK; FRACTURES WITH SLICKENSIDES; SHELL MATERIAL
●	YELLOW:	LIMESTONE TO CA-RICH SAND; GRADATIONAL MUDROCK/CARBONATE CONTACT IN CORE 1
●	DARK GREY:	SIDERITE LAYERS





The Smithwick Formation is an Early Pennsylvanian unit that was deposited in the Fort Worth Basin predominantly consisting of mudrock. The Smithwick overlies the carbonate Marble Falls Formation and is beneath the Atoka Shale and Strawn Formations. Two cores that penetrated the Smithwick Formation from the southern Fort Worth Basin were analyzed for their elemental chemistry.

GRAPHICAL INTERPRETATIONS:

- The Si/Al plots for both cores identify different intervals of the core with varying chemistry
  - An Al-rich zone (black symbols) produces a group that signifies a transition in clay composition
  - Two muddy carbonate groups (yellow and dark grey symbols) are also evident
    - The siderites form (dark grey) a more defined carbonate group
    - The limestone group (yellow) is more defined in Core 2; whereas, the interfingering of the Marble Falls and Smithwick formations in Core 1 creates a gradational carbonate-mudrock transition that is also evident in the chemostratigraphy
  - The intervals that are predominantly mudrock plot in the same vicinity with some variation
- %Al can be used a proxy for clay
  - The Marble Falls unit at the base of both cores shows a depletion of %Al, because the formation is predominantly carbonate
  - The high-Al, or clay-rich, interval is present in both cores and is a useful zone for correlation
- The %Si decreases in both cores where they are Ca-rich or Al-rich
  - There is not a large increase in %Si in the mudrock portions of the cores suggesting that biogenic silica is not a significant component of the strata
  - There is a slight overall increase in % Si above the Al-rich layer in both cores which differentiates the overlying mudrock from the Smithwick
- The Ca-enrichment in the lower portions of both cores can be used to identify the Ca-carbonate lithology associated with the Marble Falls
  - The is also an interval (red) in Core 2 where the mudrock is being diluted by calcium
- The dominant clay composition associated with the mudrock in both cores is Fe-enriched
  - The baseline created from the %Fe plots illustrates the Fe that is associated with the clays
  - The spikes in %Fe (also evident in other elements) are indicative of siderite layers

BOSSIER/HAYNESVILLE CHEMOSTRATIGRAPHY
JURASSIC, EAST TEXAS BASIN
(CORE LOCATION IS PROPRIETARY INFORMATION)