Abstract

Shale resource plays are becoming increasingly important within the petroleum industry both in the U.S. and globally. However, understanding how shales change both temporally and spatially with respect to mineralogy and depositional environment, and assessing how these changes may relate to reservoir quality are not well understood. In recent years, inorganic elemental analyses have been routinely applied to many shale plays to better understand mineralogy, stratigraphy, and depositional environment, with this approach being particularly effective within Eagle Ford and Haynesville formations. In this study, results are presented from inorganic elemental analyses from a series of Appalachian shales including Marcellus and Burket sequences in order to explore if this approach can provide useful insights in a relatively carbonate-poor shale system.

Data for up to 50 elements have been acquired from core and cutting samples from wells drilled in Tioga County, Pennsylvania. The results of these analyses are discussed in conjunction with stratigraphic data, TOC and XRD analyses to provide an integrated stratigraphy and characterization of these sections.

Several elements and elemental ratios such as Ca/Al, Th/U, K/Rb, Na/Al, Zr/Al, Al/bases and U show significant vertical changes through the study intervals. They allow each sequence to be subdivided into several broad-scale chemostratigraphic packages and higher resolution units that are correlated to produce a robust chemostratigraphic correlation framework within this area. Furthermore, these ratios provide helpful insights into various processes, since they reflect lithological changes (Ca/Al), grain size (Zr/Al), potential provenance change (Na/Al and K/Rb), and variations in environmental conditions (U, Al/bases).

In addition to classic chemostratigraphy, this study also demonstrates how inorganic whole rock geochemical data can be used to determine paleoredox facies, model mineralogy and TOC contents, and be used to estimate biogenic silica contents.
Paleoredox conditions play an important role in determining organic matter preservation and consideration of redox-sensitive elements, such as V, Ni, Th, U, and Mo provides a means to determine the degree of anoxia during deposition. Major element concentrations can be used to model most mineral phases, and by incorporating select trace elements, typically U and Ni, TOC content can also be modeled. These models are compared to XRD and measured TOC values to demonstrate the efficacy of this methodology.

Although it is appreciated that all shale plays have different characteristics, the applications of inorganic elemental data outlined in this study are readily exportable to any shale resource play. Information generated from this type of dataset may be tailored to a number of different uses from regional correlations to aiding in lateral well completions.

Reference Cited

Effective Application of Inorganic Geochemical Data in Shale Resource Plays: A Case Study from the Appalachian Basin

Nahysa Martinez and Milly Wright – Chemostrat Inc.

Andrea Reynolds – Shell
Introduction

Marcellus–Burkett Characterization

Correlation in Tioga County, PA

Units Correlation in Marcellus Shale

Geochemical Modeling and Assessment:

- Mineralogy
- Redox
- Depositional environments

Conclusions
In the past decade, shale resource plays have risen to the forefront of hydrocarbon exploration.

However, the fine grained, macro-scale homogeneity of many formations currently being exploited, negates some of the more traditional approaches to reservoir characterization and stratigraphic correlation.

In this study the application of inorganic whole rock geochemical data to Middle Devonian shale sequences within a small area of the Appalachian Basin in northern Pennsylvania is used to both characterize and provide a robust correlation framework for these sequences.
Study Area, Samples & Analysis

- Study includes 21 wells
- Study interval includes both Marcellus and Burkett target shales
- Data acquired from 929 Cuttings and 193 Core
- Bulk elemental data from XRF and ICP OES/MS analytical techniques
- Supplementary data in this study includes XRD and TOC datasets

The focus of this study is local characterization within the Tioga Co. area
### Chemical Characterization

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<th>Depth</th>
<th>GR</th>
<th>Th/U</th>
<th>Ca/Al</th>
<th>Mg/Ca</th>
<th>K/Rb</th>
<th>Na/Al</th>
<th>Zr/Al</th>
<th>U/Al</th>
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<td>0.025</td>
<td>0.04-0.067</td>
<td>120</td>
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</tbody>
</table>

#### P1 – Low Th/U, High U

#### P2 – Higher K/RB, Th/U

#### P3 – Higher Mg/Ca, lower P

#### P4 – High Ca/Al and K/Rb

#### P5 – Lower K/Rb, P, and Na/Al

#### P6 – High Th/U and Zr/Al
Comparison with Lithostratigraphic Tops

<table>
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<th>Depth (ft)</th>
<th>GR</th>
<th>AP</th>
<th>Th/U</th>
<th>Ca/Al</th>
<th>Mg/Ca</th>
<th>K/Rb</th>
<th>Na/Al</th>
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Well A Scale: 1:2000

Upper Burkett
Lwr/Mid Burkett
Tully
Hamilton
Marcellus
2-well Correlation
2–well Correlation

Well A

Well B
Multiple Well Correlation
Multiple Well Correlation
Can recognize 9 correlative units within Marcellus Fm in the Tioga Co area
Mineralogical Controls on Elemental Chemistry

133 samples analyzed by XRD – this allows elemental and mineralogical data to be compared for a better understand of the mineralogical controls on this dataset.
Ca/Al Used as a proxy for carbonate content

U Redox sensitive & associated with organic material

Mg/Ca Although Mg can be related to dolomite, in this study it is related to clay mineral contents. This ratio is used as a proxy for clay vs. carbonate content.

P Apatite (Likely biogenic within Packages 1&5)
Mineralogical Controls on elements and ratios used for correlation within the study intervals

Terrigenous controls and Detrital composition:

Th/Al  ➔  Thought to be related to changes in clay mineral types

Na/Al  ➔  Used as a proxy for plagioclase contents

K/Al  ➔  Related to changes in clay mineral species
 – K is commonly used as a proxy for illite contents in shales

Zr/Al  ➔  Used as a proxy for Zircon contents and may also be used as a grain size proxy

Fe/Al  ➔  Pyrite (P1&P4) or Chlorite (other packages) vs. Clays contents
**EF (enrichment factor):**

$$EF_{El} = \frac{El/Al_{Sample}}{El/Al_{PAAS}}$$

EFV Values of 1 or less are indicative of a mudrock deposited in oxic / sub oxic conditions, whereas values of over 1 imply authigenic enrichment in anoxic conditions (Tribovillard et al., 2006).
**EF (enrichment factor):**

\[ EF_{EI} = \frac{E_{I}/A_{I, \text{Sample}}}{E_{I}/A_{I, \text{PAAS}}} \]

EFV Values of 1 or less are indicative of a mudrock deposited in oxic / sub oxic conditions, whereas values of over 1 imply authigenic enrichment in anoxic conditions (Tribovillard et al., 2006).
Looking for a TOC proxy within the elemental dataset
Paleoenvironmental Indicators – Redox

P1–Marcellus Example
Marcellus compared to other Shale Plays
Marcellus compared to other Shale Plays
Marcellus compared to other Shale Plays

![Diagram showing comparison of Marcellus to other shale plays with biogenic and detrital trends.]
Marcellus compared to other Shale Plays
Marcellus compared to other Shale Plays
Conclusions

- Chemostratigraphy has been successfully applied to Middle Devonian shale sequences in the Appalachian Basin to characterize, correlate, and elucidate various geological processes.

- Although each shale play tends to have its own unique characteristics, the techniques and methodologies used here are readily exportable to other shale resource plays both in the US and around the world.