ASSESSMENT OF NATURAL GAS PRODUCTION POTENTIAL IN THE DEVONIAN MARCELLUS SHALE OF PENNSYLVANIA

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Importance of Natural Gas

- Currently supports 20% of U.S. energy requirements
- At present usage rate the Marcellus could supply domestic gas needs for up to 56 years
- Reduce dependence on foreign energy

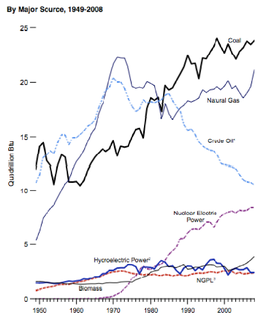

Figure 1. Energy consumed in the U.S. by source from 1949-2008

Hypothesis

Time series trends within the Marcellus will produce peaks in TOC that will correspond with excursions in $\delta^{13}C$, $\delta^{34}S$, and $\delta^{15}N$

Geologic Setting

The Marcellus Formation is a sedimentary rock unit in the Appalachian basin of the eastern United States. It is composed primarily of black shale, the result of a high concentration of preserved organic matter. The Marcellus Fm. was deposited over 380 Ma in the Middle Devonian Period when eastern Laurentia was located 15-30° south of the equator (Werne 2002).
Sediments eroded from the Acadian orogenic belt accumulated in the continental deep-water basin as transgressive and regressive depositional sequences.

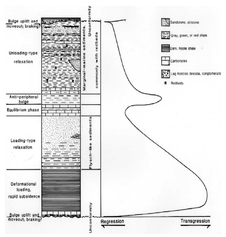

Figure 2. Sedimentary response to flexural downwarping of Laurentian coast

Comparative Analysis

- Devonian aged shales from other Laurentian basins display similar trends in carbon and sulfur elemental and isotopic abundances
- $\delta^{13}C$ values from the New Albany shale of the Illinois basin range from -19‰ to -30‰, and TOC values range from 1% to 12% (Hailer 1982)
- $\delta^{34}S$ values range from -3‰ to -30‰ and total S values range from 1% to 6% (Hailer 1982)
- Carbonate $\delta^{13}C$ values range from -1‰ to -10‰
- Similarities across multiple basins represent depositional conditions that were common throughout Laurentia

Experiment Design

Unexposed hand samples were collected at 2 m intervals from an outcrop in Kistler, PA. Dip angles were measured along the outcrop to calculate a height of 112 m ± 22.5

Samples were crushed into bulk powders with a mortal and pestle and several were tested for the presence of carbonate with 25% HCl

The samples were then weighed and analyzed using a Eurovector elemental analyzer and GV Instruments gas source mass spectrometer

NIST standards Urea, NBS-19, and NBS-127 were used to measure elemental and isotopic abundances of C, S, N, $\delta^{13}C$, $\delta^{34}S$, $\delta^{15}N$, and $\delta^{18}O$

Figure 3. Marcellus outcrop in Kistler, PA. Outcrop height is approximately 12 m.

Standard	Weight %	Isotopic Abundance (‰)
NBS-127 (Barium Sulfate)	S – 13.47	$\delta^{34}S$ +21.1
Urea	C – 20	$\delta^{13}C$ -29.39
	N – 47	$\delta^{15}N$ +1.18
NBS-19 (Limestone)	C – 12	$\delta^{13}C$ +1.95
	O – 48	$\delta^{18}O$ -2.2

Figure 4. Standards used with elemental and isotopic abundances

Results

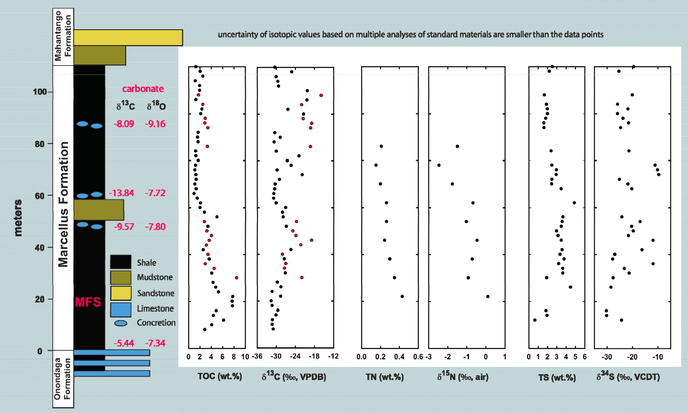

Figure 5. Stratigraphic column of the Marcellus Fm. with plots of TOC, $\delta^{13}C$, %S, $\delta^{34}S$, %N, and $\delta^{15}N$. Red data points represent samples that were analyzed with carbonate present. MFS = maximum flooding surface.

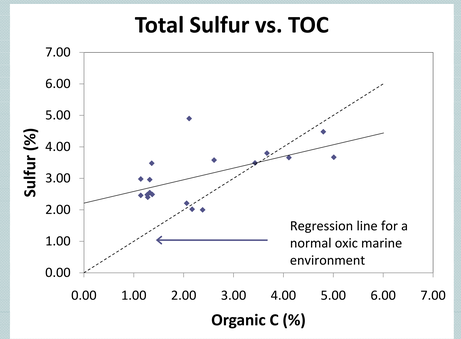

Figure 6. Total sulfur vs. organic carbon. The solid linear regression line represents the Marcellus with anoxic bottom waters, and the dashed line represents a normal oxic marine environment (from Leventhal 1983).

- TOC values in the upper half of the formation were consistently low, but after 50 m steadily increased down section to 8.9% ± 1.2
- $\delta^{13}C$ data scattered above 65 m, more depleted down section
- Total N steadily increased down section to 0.43% ± 4.4 14 m above the base
- $\delta^{15}N$ enriched down section, most enriched 14 m above the base
- Total S increases slightly toward base, but appears to drop just above the base
- $\delta^{34}S$ data scattered with large variation, most depleted 8 m above base
- Linear regression line through S/C graph intercepts S axis

References

Hailer, J. G., and R. K. Leininger., 1982, Sulfur And Carbon Isotope Trends in the New Albany Shale (Devonian and Mississipian) In Indiana, Eastern Oil Shale Symposium v. 75, p. 127-35.
Leventhal, J.S., 1987, Carbon and Sulfur Relationships in Devonian Shales From the Appalachian Basin as an Indicator of Environment of Deposition: American Journal of Science, v. 287, p. 33-49.
Werne, J.P., Sageman, B.B., Lyons, T.W., Hollander, D.J., 2002, An Integrated Assessment of a "Type Euxinic" Deposit: Evidence for Multiple Controls on The Middle Devonian Oatka Creek Formation, American Journal of Science, v. 302, p. 110-143.

Sources of Uncertainty

- Dip angle of bedding ranged from 8° to 12°
- Differences between elemental composition of samples and standards
- Initial acid test revealed no carbonate, bulk powders used for analysis

Maximum Flooding Surface

- The maximum flooding surface marks the farthest landward extent of deep water facies and terminates the transgressive depositional sequence
- 12 m above the base of the Marcellus likely represents the maximum flooding surface (Fig. 2)
- Highly depleted values of $\delta^{34}S$ and $\delta^{13}C$, a linear regression line intersecting the S axis on the S/C graph, and the highest concentration of organic matter are all consistent with an anoxic marine depositional environment associated with the maximum flooding surface
- This horizon is ideal for natural gas exploration because it is a source rock, and the impermeable shale provides a seal to trap any oil or gas generated

Conclusions

- Trends within the Marcellus reveal one strong peak in TOC that corresponds with peaks in S and N, enriched $\delta^{15}N$, depleted $\delta^{13}C$, and depleted $\delta^{34}S$
- These data are not consistent with my hypothesis that TOC peaks will correlate with significant excursions in carbon isotope data, although there appears to be changes in ^{34}S and ^{15}N abundances associated with the maximum flooding surface
- The horizon 12 m above the base of the Marcellus represented by the maximum flooding surface has the greatest potential for natural gas production

Acknowledgments

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