

**PS Sediment Provenance Study of the Lower Hamilton Group:  
An Analysis of the Organic-Rich Facies and its Depositional History\***

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**Abstract**

Currently, no geological model exists to explain the variability and distribution of organic-rich facies in the Marcellus Shale. Within the central Appalachian basin, there are two “sweet spots”, one in Northeast Pennsylvania and another in Southwest Pennsylvania/North-Central West Virginia. In these areas, the Marcellus Shale contains thick accumulations of organic matter and are highly productive for natural gas. In contrast, many studies and production reports have shown that in other areas, the Marcellus Shale is relatively organic-poor. One possible explanation for the lower organic content is that detrital dilution was greater in these areas compared to surrounding productive regions. This hypothesis will be tested by analyzing the provenance of inorganic detritus in the Marcellus Shale. Recent study of the MSEEL (Marcellus Shale Energy and Environmental Laboratory) well in north-central West Virginia revealed input from the Superior Craton decreased and input from the Acadian mountains increased as TOC in the Marcellus decreased up-section. This suggests detrital dilution of organic matter should exert a decreasing influence southward along the basin axis. To examine this idea further, a comparison will be made between the MSEEL well and two wells located in other areas of the basin. Facies classifications and provenance interpretations will be made in the Marcellus Shale intervals based XRD mineralogy and XRF/ICP-MS major/trace element geochemistry. These data will be combined with Sm-Nd analysis to further constrain provenance. Raman spectral analysis will be used to evaluate thermal maturity and its relationship to organic richness of Marcellus facies. Ultimately, these data will be used to model the depositional environments, sediment provenance, and thermal maturity to explain the variation in organic matter content in the central Appalachian Basin.



# Sediment Provenance Study of the Lower Hamilton Group: An Analysis of the Organic-Rich Facies and its Depositional History

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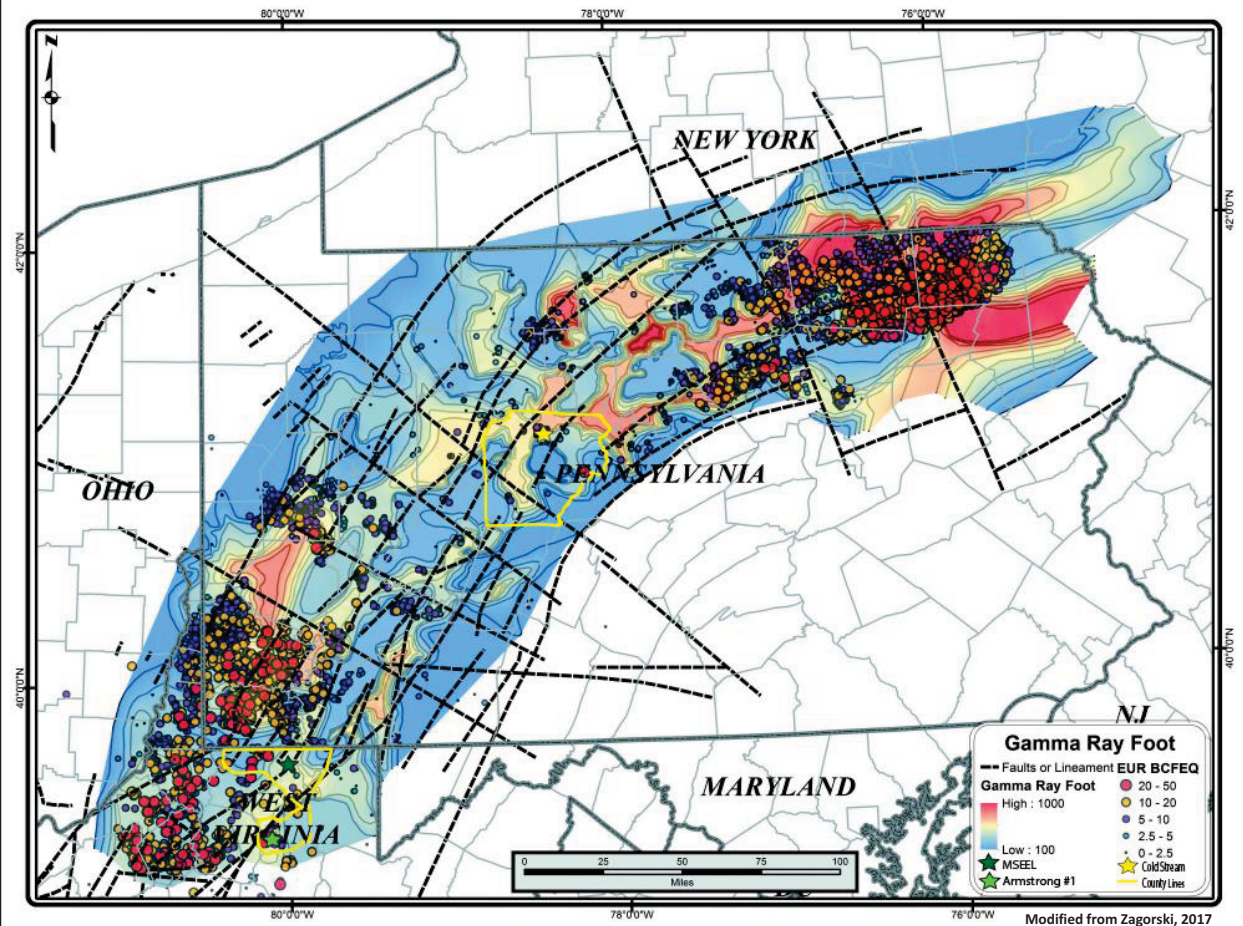
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## Abstract

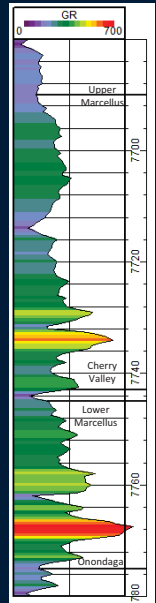
Currently, insufficient geological models exist to explain the variability and distribution of TOC in the Marcellus Shale, within the Hamilton Group. TOC is one of the several limiting factors for natural gas production within the Marcellus Shale basin. One possible explanation for the low TOC regions is that detrital dilution was variable across the basin, with different sediment sources contributing detritus to low TOC areas, compared to surrounding regions with higher TOC. This hypothesis is tested by analyzing the source composition of inorganic detritus, using elemental and mineralogical proxies, with two cores in the Hamilton Group. The Armstrong #1 core is located in Taylor County, West Virginia and the Coldstream Affiliates 1MH (CSA) core is located in Clearfield County, Pennsylvania. Both these wells are located outside of the higher productivity regions with a nearby horizontal Armstrong well totaling 0.45 BCF/1000ft lateral and a nearby horizontal CSA well totaling 0.41 BCF/1000ft lateral. Variation in production may also result from over maturation of the kerogen-hosted pores. To evaluate the influence of thermal history, the thermal maturity of the Marcellus Shale in the lower productivity Armstrong #1 and CSA wells and the higher productivity MSEEL well was assessed using Raman spectroscopy.

Major element, trace element, and REE geochemistry indicate the sediment source area was composed of intermediate and felsic granitic and recycled sedimentary lithologies. Samarium-neodymium isotopic analysis reveals a range of  $\tau_{DM}$  ages and  $\epsilon_{Nd}$  values. The Armstrong #1 well  $\tau_{DM}$  /  $\epsilon_{Nd}$  ranged from 1.64 to 1.91 Ga / -11.93 to -9.56 and the CSA from 1.62 to 1.88 Ga / -12.07 to -11.12. The  $\epsilon_{Nd}$  values became more negative upsection, however the  $\tau_{DM}$  did not display a consistent trend relative to depth. Provenance analysis indicates the most likely source of clastic sediment was the Acadian Fold-Thrust Belt to the east with minor inputs from Superior Craton and southern Canadian Grenville Province. Ultimately, results conclude that elevated TOC was associated with only older  $\tau_{DM}$  ages and recycled sedimentary signatures.

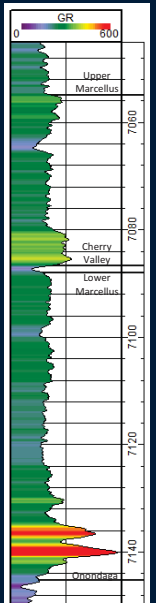
## Well Locations



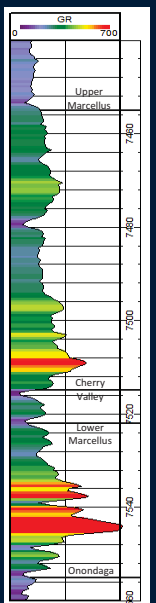
## Armstrong Well



## Coldstream Well



## MSEEL



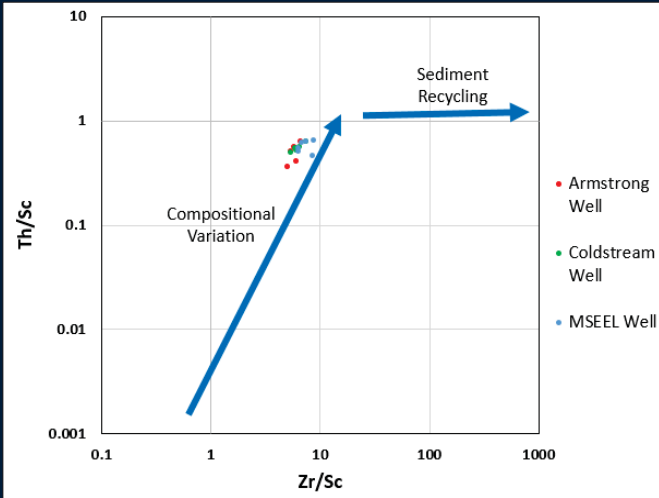
## Sm/Nd Results

Samarium and neodymium isotopes were extracted from powdered core samples of the Armstrong and Coldstream wells. The isotopes were measured using a TIMS (Thermal Ionization Mass Spectrometer) at the University of Alabama Radiogenic Isotope Lab for the Armstrong and Coldstream wells. The MSEEL well isotopes were provided by Hupp (2017).  $^{143}\text{Nd}/^{144}\text{Nd}_{DM} = 0.51315$ ,  $^{147}\text{Sm}/^{144}\text{Nd}_{DM} = 0.2137$ ,  $^{143}\text{Nd}/^{144}\text{Nd}_{CHUR} = 0.512638$ , and  $^{147}\text{Sm}$  decay constant ( $\lambda$ ) =  $6.54 \times 10^{-12}$ .

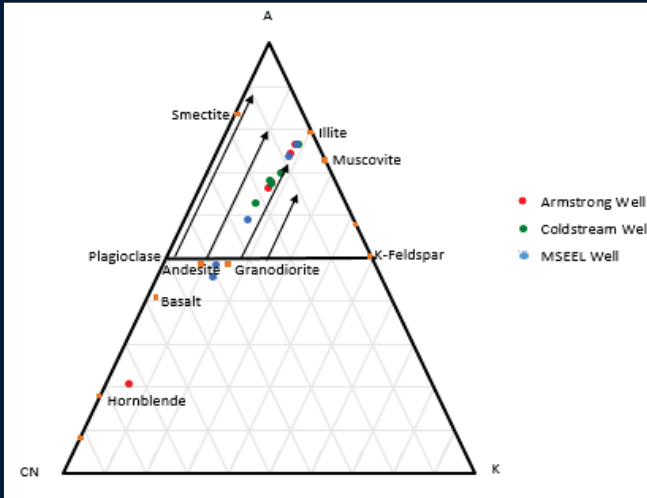
Armstrong			Coldstream			MSEEL		
Depth	$\epsilon_{Nd}$	$\tau_{DM}$ Ga	Depth	$\epsilon_{Nd}$	$\tau_{DM}$ Ga	Depth	$\epsilon_{Nd}$	$\tau_{DM}$ Ga
7660	-11.83	1.65	7032	-11.61	1.88	7448	-10.34	1.85
7670	-11.45	1.64	7060	-11.12	1.84	7460	-10.51	1.79
7705	-11.20	1.80	7075	-12.07	1.62	7489	-10.55	1.63
7730	-10.05	1.91	7110	-11.43	1.68	7506	-10.18	1.81
7760	-9.56	1.76	7144	-11.39	1.76	7538	-9.85	1.78

## ICP-MS/ICP-OES/XRF Results

Core chips from the Armstrong and Coldstream wells were crushed and sent for elemental analysis using ICP-MS. Handheld XRF data on the Armstrong and Coldstream collected by NETL supplemented the ICP-MS data. Data from Hupp, 2017 on the MSEEL well were used to compare to the elemental results of the Armstrong and Coldstream wells. The comprehensive data were used for sediment source composition calculations and detrital influence indicators.

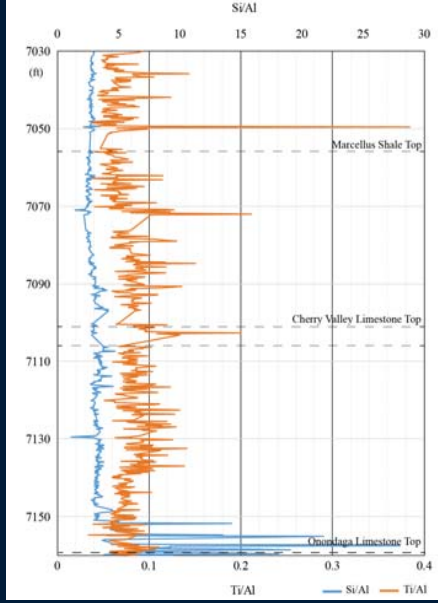


Incompatible elements, thorium and zirconium, were compared to scandium concentrations to investigate the sediment source composition according to McLennan *et al.*, 1993.

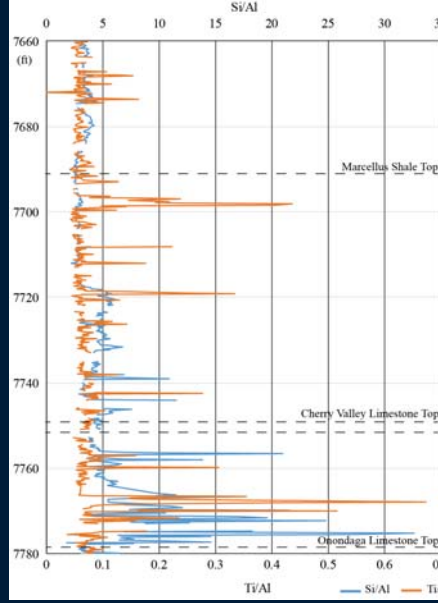


Aluminum (A), calcium and sodium (CN), and potassium (K) concentrations were used as another method to assess source composition according to Nesbitt and Young, 1989.

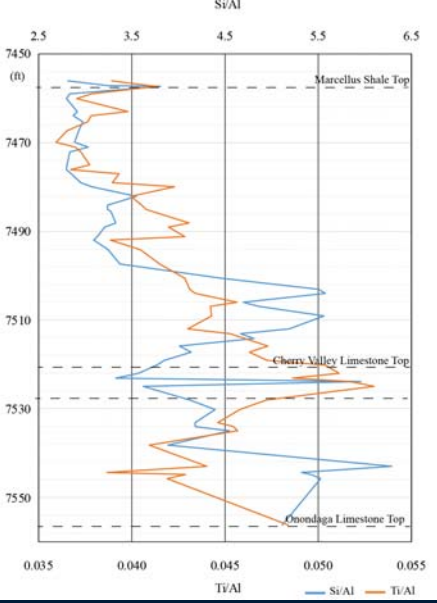
## Coldstream Well



## Armstrong Well



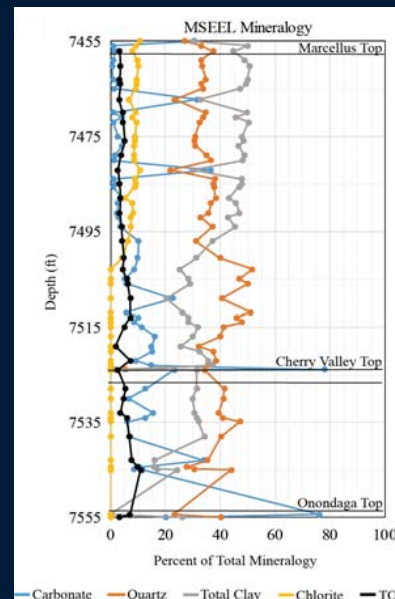
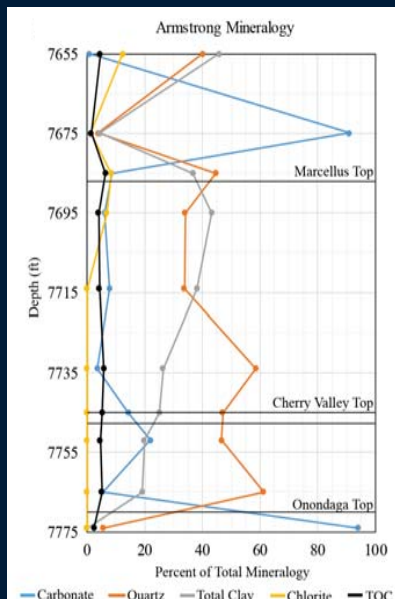
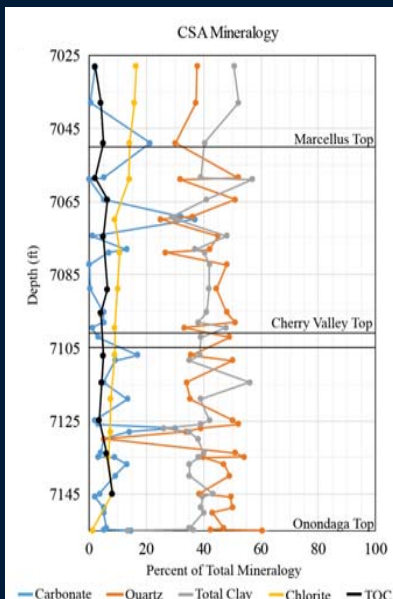
## MSEEL Well



Si/Al is used as a proxy for detrital dilution. A lower ratio indicates detrital dilution because aluminum is prevalent in clay minerals, which are common detritus. (Sageman *et al.*, 2003) Ti/Al is used as a proxy for eolian silt influx. A high ratio indicates eolian silt such as rutinated quartz. Enrichment in eolian silt indicates sediment starvation during deposition. (Sageman *et al.*, 2003)

## XRD Mineralogy Results

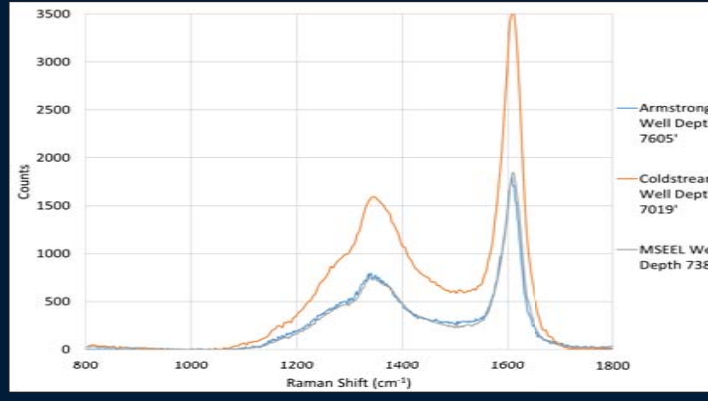
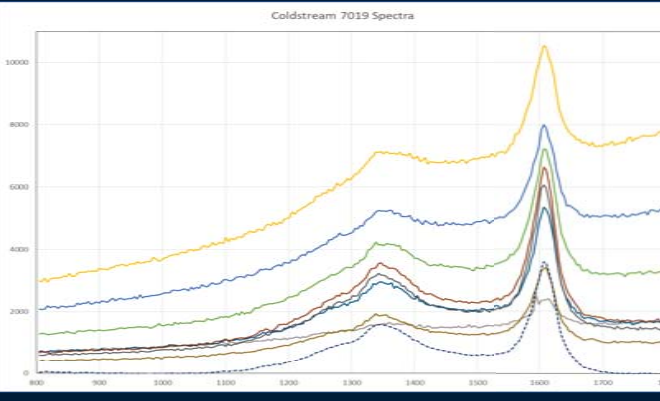
XRD analysis was analyzed by Core Laboratories on the Armstrong and Coldstream wells. XRD analysis on the MSEEL well was provided by Hupp, 2017.



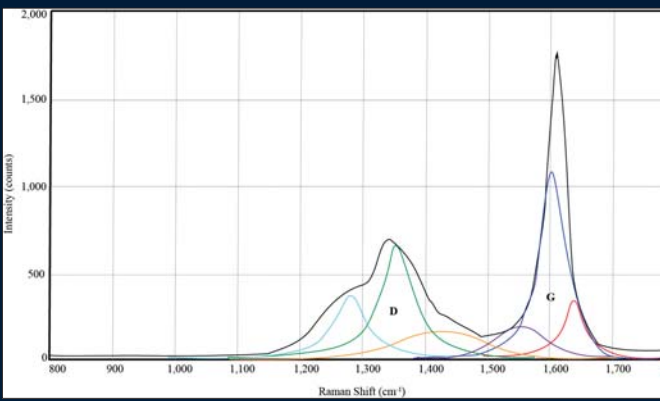
## Raman Spectral Analysis

Raman spectroscopy is an efficient and inexpensive technique when compared to vitrinite reflectance ( $VR_o$ ). Raman spectra from the carbon bonds of organic matter in black shales show a D-band (disordered band) and a G-band (graphic). With increasing thermal maturation the separation between the D-band and the G-band increases (Lupoi *et al.*, 2017).

Raman spectra were acquired from core chips, at depths where  $VR_o$  was measured, from Taylor County, WV (average TOC of 4 wt%) and Clearfield County, PA (average TOC of 4 wt%). The Taylor County  $VR_o$  averaged around 1.4% and the Clearfield County  $VR_o$  averaged around 2.7%. Raman Spectral acquisition parameters were: a 473 nm laser, ND filter of 1%, 600 grooves/mm, a pinhole size of 200  $\mu\text{m}$ , and an acquisition time of 5 seconds. Raman spectra from these lower TOC regions were compared to the higher TOC (average TOC of 6 wt%) Marcellus Shale of the MSEEL (Marcellus Shale Energy and Environmental Laboratory) well in north-central WV, where  $VR_o$  was not observed. The MSEEL well is speculated to have a lower thermal maturity than the Clearfield County well, making it within the ideal thermal maturity range. Analysis revealed that the D and G-band frequencies for the MSEEL well are closer relative to the Coldstream well in Clearfield County.



Spectra acquired from a Coldstream core chip at 7019'. All have relatively similar peak morphology. Coldstream G- and D-bands are slightly shifted.



A six-peak fit of the CSA well at depth 7099'. D- and G-bands are labeled where values are used.

Comparison of spectra from the three test wells. Coldstream G- and D-bands are slightly shifted.

MSEEL		Coldstream		Armstrong	
Depth	G-D $\text{cm}^{-1}$	Depth	G-D $\text{cm}^{-1}$	Depth	G-D $\text{cm}^{-1}$
7475	252.19	7019	252.27	7605	247.95
7477	252.48	7070	254.5	7655	248.91
7494	251.25	7099	254.5	7714	251.05
7534	247.39	7128	249.96	7752	249.54
7556	250.00	7155	249.25	7765	249.39
Average	250.66	Average	252.10	Average	249.37

The G-band frequency was subtracted by the D-band for each sampled depth in the three wells.

## Conclusions

The high elemental variation and the geographic location of the Armstrong well suggest that detrital dilution had a role in its productivity. The Armstrong well is located closer to where the Acadian Mountains would have been located. The Acadian Mountains provided a majority of the source material that would dilute the organic carbon that was produced. The elemental variation could be attributed to pulses of sediment come the Acadian Mountains. Also, the source composition figures indicate that the Armstrong Well sourced more from more immature rocks such as diorites and granodiorites. This indicates that detrital dilution could have played a more substantial role because immature sediments are generally closer to the source than more mature sediments.

However, in the Coldstream well, over-maturity and clay dominance are feasible limiting factors for production. Over-maturation leads to degradation of the kerogen-hosted porosity. The Coldstream well's  $VR_o$  of 2.7% and G-D band frequency average of  $\sim 252 \text{ cm}^{-1}$  indicate over-maturation. Clay dominance can affect the quality of a hydraulic fracturing job, which can lead to overall less production.

The  $\tau_{DM}$  ages indicate that there was likely a mixing of older sediments from the accreted terranes (such as the Algonquia or Barillia terranes) in the Grenville province with younger sediments in the Acadian fold-thrust belt. There is no evidence of a Devonian basin forming in northern New York, eastern Ontario, and southern Quebec; the lack of accommodation allowed for the sediments to travel into the Acadian basin where the three wells are located (Fail, 1985).

## Future Work

A more robust  $VR_o$  proxy model using Raman spectroscopy and multivariate analysis is currently being developed by RJ Lee Group and will provide another approach to estimating thermal maturity.

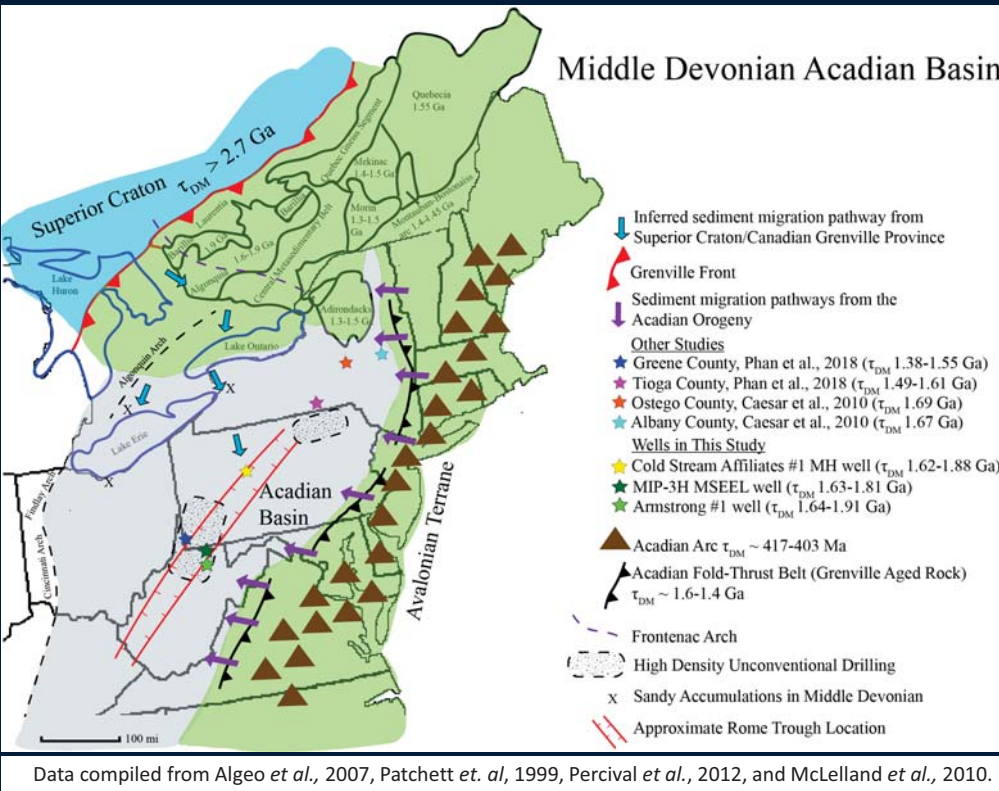
Sm/Nd isotopes in other locations of the basin are needed for a more complex depositional model.

## Acknowledgments

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## Sediment Provenance Possibilities



## Sediment Provenance Equations

Equation 1:

$$\tau_{DM} = \frac{1}{\lambda} \ln \left( \frac{^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}} - ^{143}\text{Nd}/^{144}\text{Nd}_{DM}}{^{147}\text{Sm}/^{144}\text{Nd}_{\text{sample}} - ^{147}\text{Sm}/^{144}\text{Nd}_{DM}} + 1 \right)$$

Equation 2:

$$\epsilon_{Nd} = \left[ \frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}} - (^{143}\text{Nd}/^{144}\text{Nd})_{CHUR}}{(^{143}\text{Nd}/^{144}\text{Nd})_{CHUR}} \right] \times 10000$$

(Dickin, 2009)