[PS]High Resolution XRF Stratigraphy of the Ordovician Utica Shale, Central New York State*

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Abstract

Bulk rock elemental concentrations were collected using a handheld X-ray fluorescence spectrometer at 5 mm resolution through 5 m of core collected from the Utica Shale in central New York State. These results provide a higher resolution context to previous measurements from this core taken at stratigraphic scale of 7.62 cm (3 inches). While the two datasets are consistent, higher frequency trends are now resolvable and help to better understand the "signal-to-noise ratio" of the lower frequency data that extends over a much longer stratigraphic interval. Additionally, undetected elemental trends have been recognized below the resolution of the coarser dataset.

The data collected in this study was also analyzed using a software package developed by the EPA called EPA PMF which uses positive matrix factorization, a form of multivariate factor analysis, to unmix the elemental concentrations of each sample into a set of geologically identifiable components. The stratigraphic trends in the contribution of these components can then be plotted to investigate changes in carbonate and biogenic silica content, the composition of siliciclastic detritus, and redox proxies. The results of this study suggest that short intervals of core through the various members of the Utica Shale and the associated Trenton Group limestones should be analyzed at high resolution to better understand the lower frequency datasets. By combining short intervals of high frequency data with longer intervals of low frequency data, collection rate and geologic resolution are not compromised.

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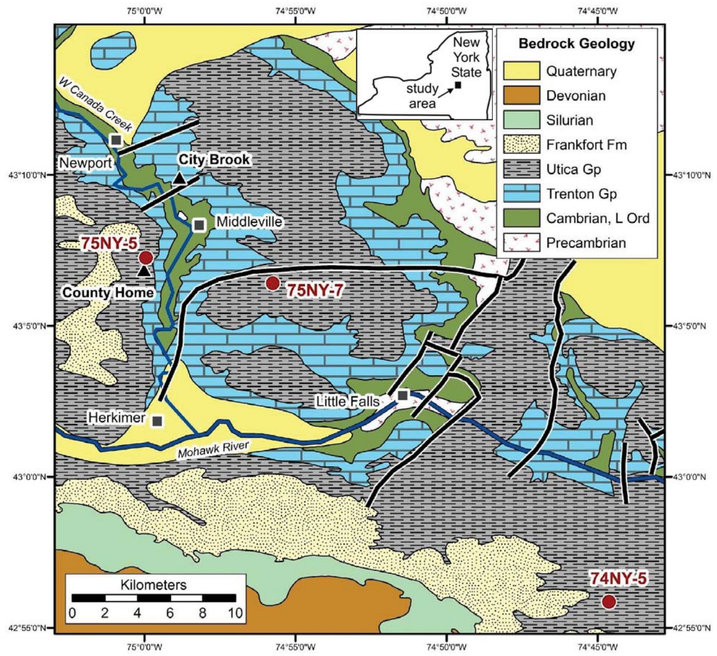
Bulk rock elemental concentrations were collected using a handheld X-ray fluorescence spectrometer at 5 mm resolution through 5 m of core collected from the Utica Shale in central New York State. These results provide a higher resolution context to previous measurements from this core taken at stratigraphic scale of 7.62 cm (3 inches). While the two datasets are consistent, higher frequency trends are now resolvable and help to better understand the "signal to noise ratio" of the lower frequency data that extends over a much longer stratigraphic interval. *Additionally, undetected elemental trends have been recognized below the resolution of the coarser dataset.* The data collected in this study was also analyzed using a software package developed by the EPA called EPA PMF which uses positive matrix factorization, a form of multivariate factor analysis, to unmix the elemental concentrations of each sample into a set of geologically identifiable components. *The stratigraphic trends in the contribution of these components can then be plotted to investigate changes in carbonate and biogenic silica content, the composition of siliciclastic detritus, and redox proxies.* The results of this study suggest that short intervals of core through the various members of the Utica Shale and the associated Trenton Group limestones should be analyzed at high resolution to better understand the lower frequency datasets. By combining short intervals of high frequency data with longer intervals of low frequency data, collection rate and geologic resolution are not compromised.

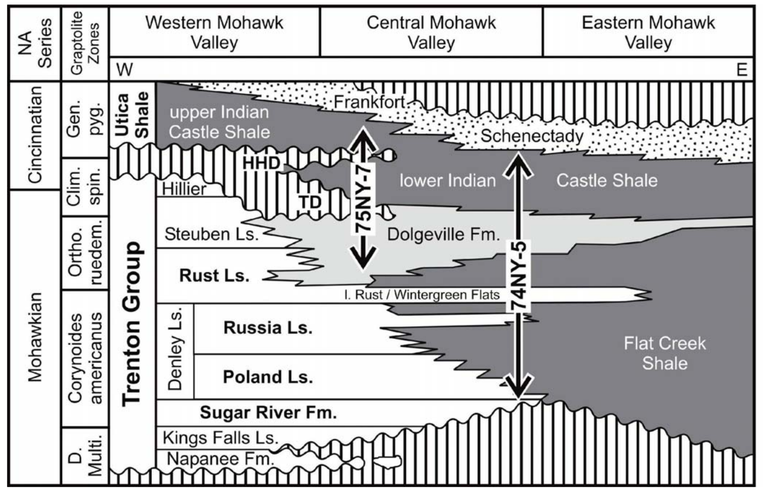
Project Aims

1. Provide high resolution elemental concentration data across a uranium cycle boundary.
2. Use higher resolution data to investigate the signal to noise ratio seen in lower resolution data sets.

Study Area and Stratigraphy



Geologic map of the study area showing core locations. Modified from Fisher et al., 1970



Chronostratigraphic chart of the Trenton Group and Utica Shale. Modified from Brett and Baird, 2002.

Study Area:

- Central Mohawk Valley of New York State
- Lower Indian Castle Shale of the Utica Group
- Deposited during Ordovician Taconic Orogeny
- 75NY-7 drill core at depth interval 50-55m

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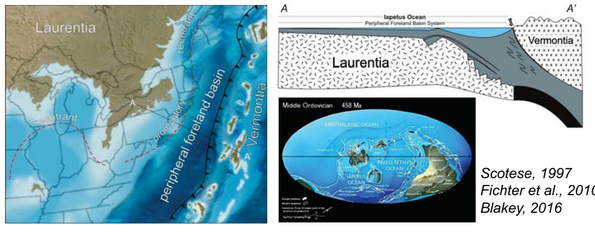
Methods

- Quantitative X-ray fluorescence spectroscopy utilized to determine bulk rock elemental concentrations of 29 elements
- Handheld Bruker TRACER III-SD
- Measured elements:
  - He analysis at 60 seconds, 15kV, 25μA:
    Mg, Al, Si, P, S, K, Ca, Ba, Ti, V, Cr, Mn
  - Yellow filter analysis at 60 seconds, 40kV, 30μA:
    Fe, Co, Ni, Cu, Zn, Ga, As, Pb, Se, Th, Rb, U, Sr, Y, Zr, Nb, Mo
- Automated data collection using a DeWitt Systems Inc. core scanning table
- XRF positioned over center of core to maximize surface area
- Collected spectrum every 5mm over 5m of core, compared to previous data set collected from same core at 3 inch intervals
- Calibrated to 41 mudstone standards (Rowe et al., 2012)

Image of handheld Bruker TRACER III-SD.

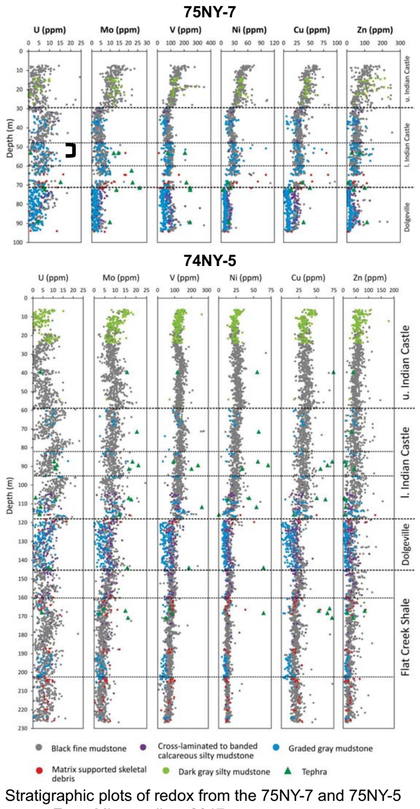
Geological Setting:

- Study location = southern tropics of Laurentia
- Basin created during the Middle and Late Ordovician Taconic Orogeny as the Iapetus Ocean closed and the Trenton carbonate platform was drowned

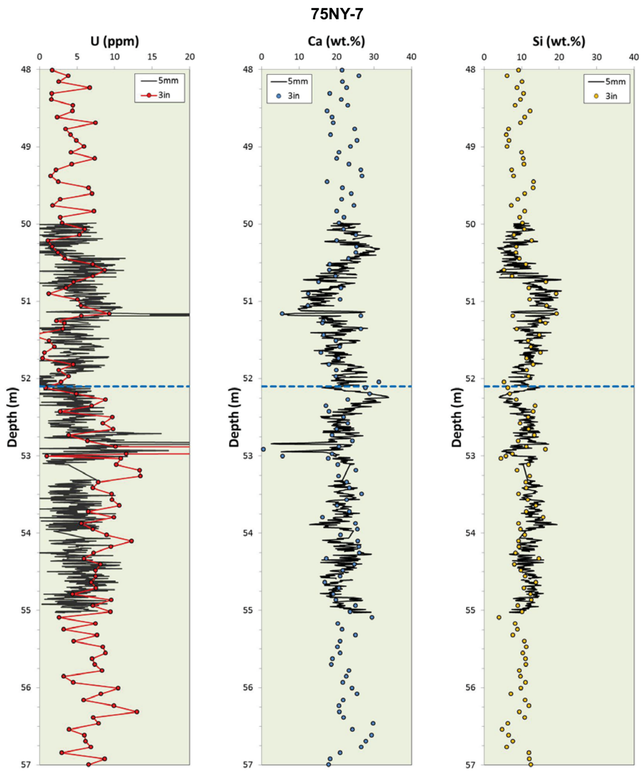


Scotese, 1997
Fichter et al., 2010
Blakey, 2016

Uranium Cycles



Stratigraphic plots of redox from the 75NY-7 and 75NY-5 cores. From Miserendino, 2017.



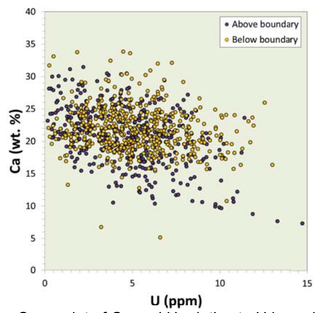
Detailed stratigraphic plots comparing high resolution and lower resolution data of 75NY-7.

Observations from Lower Resolution Data:

- Mo, V, Ni, Cu, and Zn show a stepwise upward increase indicative of increasing anoxia during drowning of the platform
- U is largely decoupled from these other redox proxies
- U cyclicity is seen in both the 75NY-7 and 74NY-5 cores throughout the Utica Group

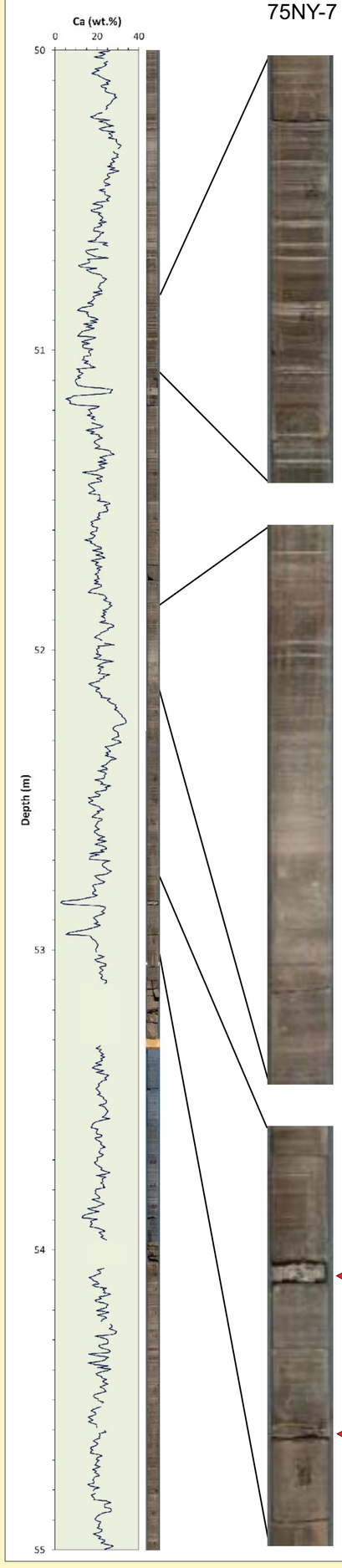
Observations from High Resolution Data:

- Project goal was to analyze one of these cycle boundaries at higher resolution (black bracket)
- Confirms occurrence of U boundary
- Calcium and silica concentrations negatively co-vary, indicating a mix of carbonate and siliciclastic lithologies
- There doesn't appear to be a direct correlation between U concentration and bulk rock minerology
- U is delivered to the sediment column by diffusion under anoxic and euxinic conditions, thus the cycles may inversely correlate to sedimentation rate



Cross plot of Ca and U relative to U boundary

Lithology



Black fine mudstones:

- Silt and clay sized grains of mixed siliciclastic and carbonate composition
- Planar laminations, no bioturbation
- Variation in color (light gray to dark gray/black) indicate variations in organic matter, carbonate, or pyrite concentrations
- Mainly low energy pelagic settling of mud
- Occasional bedload transport of white calcareous-rich sediment (likely turbidites)

Graded gray mudstones:

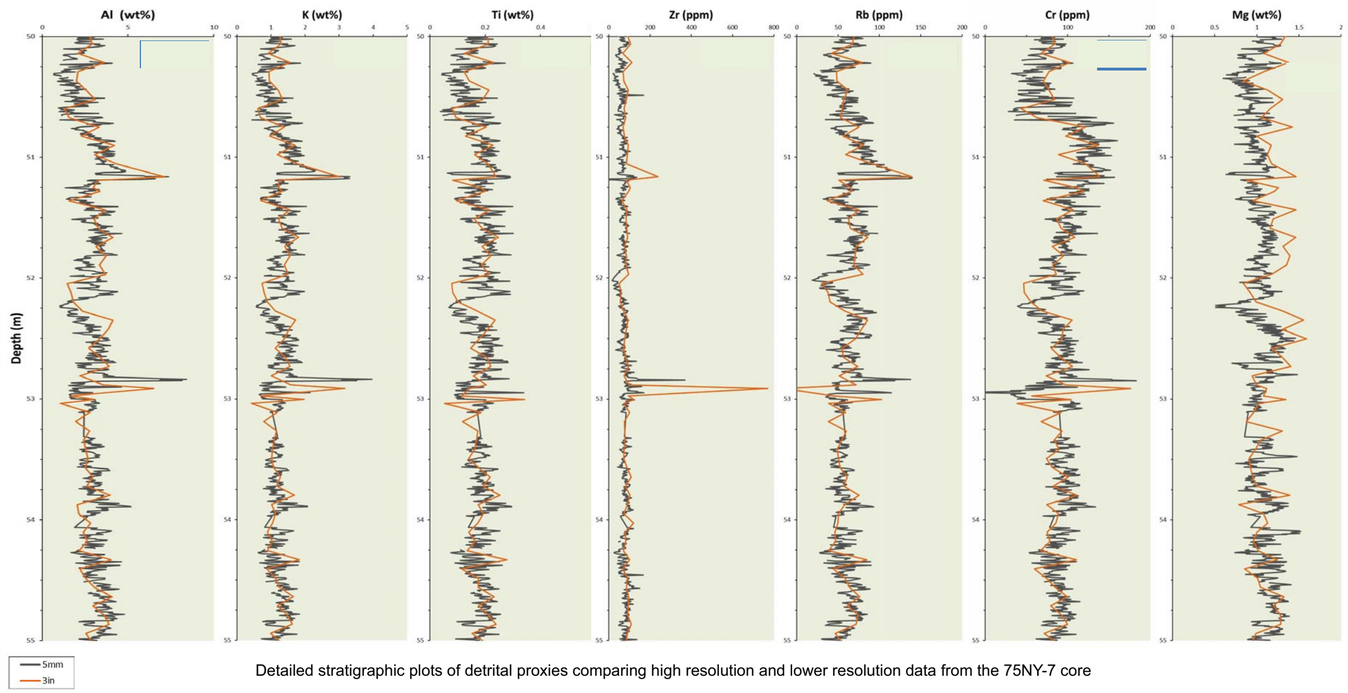
- Thicker carbonate-rich intervals commonly with sharp basal contacts and more gradual tops
- 1 to 10cm thick
- Gray to dark gray, interbedded with black fine mudstones
- Composed of calcareous mud, with fossil fragments locally at the base of beds
- Normally graded when grain size is apparent
- Low angle ripple cross-laminations and subplanar laminae in some beds
- Bioturbation is absent to moderate, but only at the top of beds when present
- Energetic turbidity current deposition

Tephra (Volcanic Ash):

- K-bentonite volcanic ash
- Thin, gray, mottled, clay rich beds of 1 to 4cm
- Typically have low Ca concentration, but high Al, Cr, K, Si, U, and Zr concentrations

Miserendino, 2017

High Resolution vs Low Resolution Data

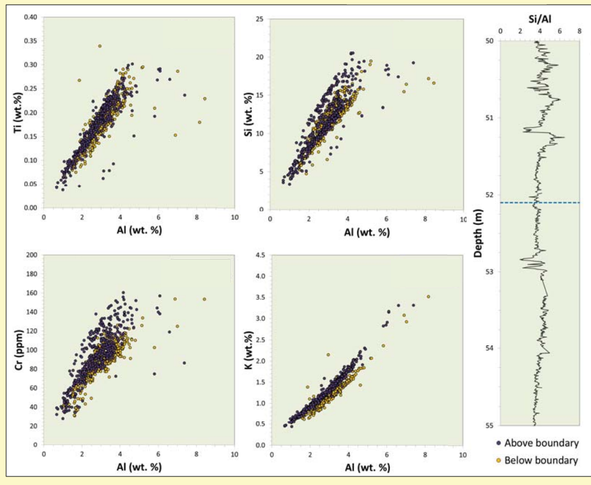


Detailed stratigraphic plots of detrital proxies comparing high resolution and lower resolution data from the 75NY-7 core

Signal or Noise?

- Is the decameter-scale scatter seen in 3 inch data significant (i.e. true signal) or is it inherent noise?
- Overall the 5mm data follows the trends and oscillations of the 3 inch data
- These oscillations are broadly replicated in 5 mm data, suggesting they are not random noise
- Thus, XRF data appears to be a very sensitive tracer of changing mineralogy

Detrital Proxies



Cross plot analysis:

- Detrital proxies are normalized to Al to remove the effects of variable carbonate dilution and investigate changes in bulk siliciclastic composition
- Detrital proxies co-vary with Al
- Ti, Si, Cr, and K show subtle changes in their abundance relative to Al below and above the U cycle boundary
- This indicates a change in the bulk composition of the siliciclastic detrital load
- Stratigraphic plot of the Si/Al ratio suggests this does not correlate with the U cycle boundary

Future Work

Suggested Future Work:

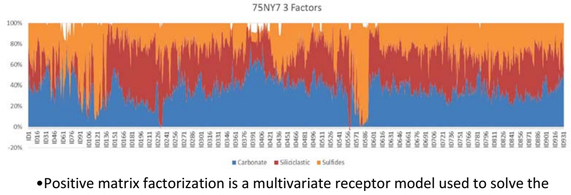
- Integrate findings with sedimentological and other proxy data for sedimentation rate
- Continue high resolution analysis above and below current extent to further explore U cyclicity
- Perform similar high resolution analysis of other boundaries identified with 3 inch data

Statistical Analysis:

- Use *EPA PMF* (positive matrix factorization) to provide an objective perspective of trends seen in this study

PMF is like unmixing cake batter to determine ingredient type and amount.

In a basin it is unmixing each source's profile.



- Positive matrix factorization is a multivariate receptor model used to solve the mass balance between bulk sample concentrations and source profiles
- Unlike PCA and FA, PMF yields positive factor profiles and concentrations allowing for geologic interpretation of results

Conclusions

- Uranium cycle boundary, and decoupling from other redox proxies seen in 3 inch data of the 75NY-7 core has been successfully replicated with high resolution 5mm data.
- Uranium concentrations do not appear to be related to changes in minerology, but may relate to variations in sedimentation rate. Low uranium concentrations would correlate to high sedimentation rates.
- XRF analysis is an effective tracer of high resolution changes in bulk rock mineralogy.
- Subtle changes in the bulk mineralogy of the detrital load, based on elemental proxies, have been identified and should be integrated with sedimentological observations.
- Previously reported lower resolution analysis of core segments from the Utica Shale, and perhaps other basins, could benefit from higher resolution data to confirm and improve geological interpretation.
- Large datasets such as these would greatly benefit from objective statistical analysis.

Acknowledgements

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