Investigating Spatial and Temporal Changes in Trace Element Abundance in Devonian Shales of Kentucky

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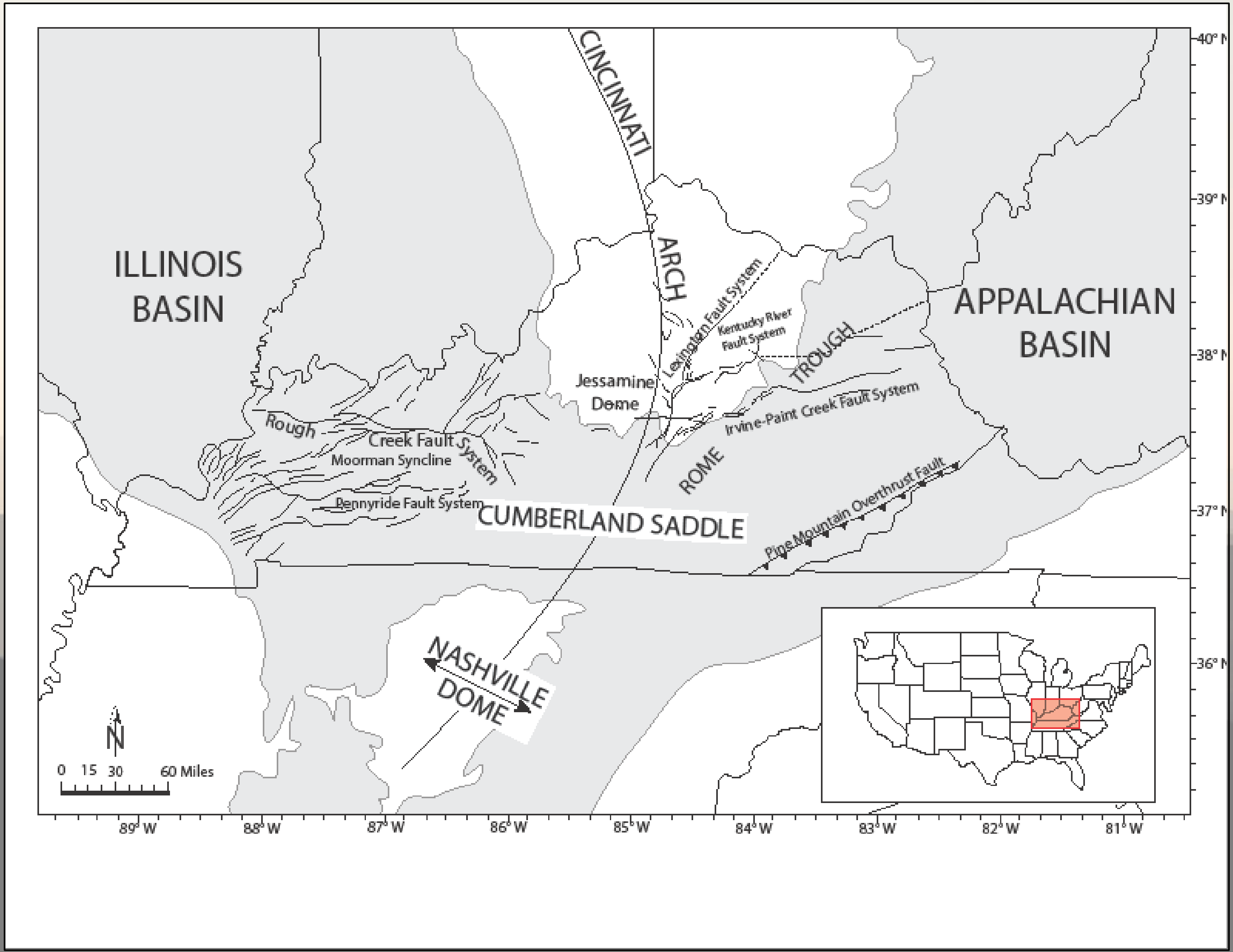
Introduction

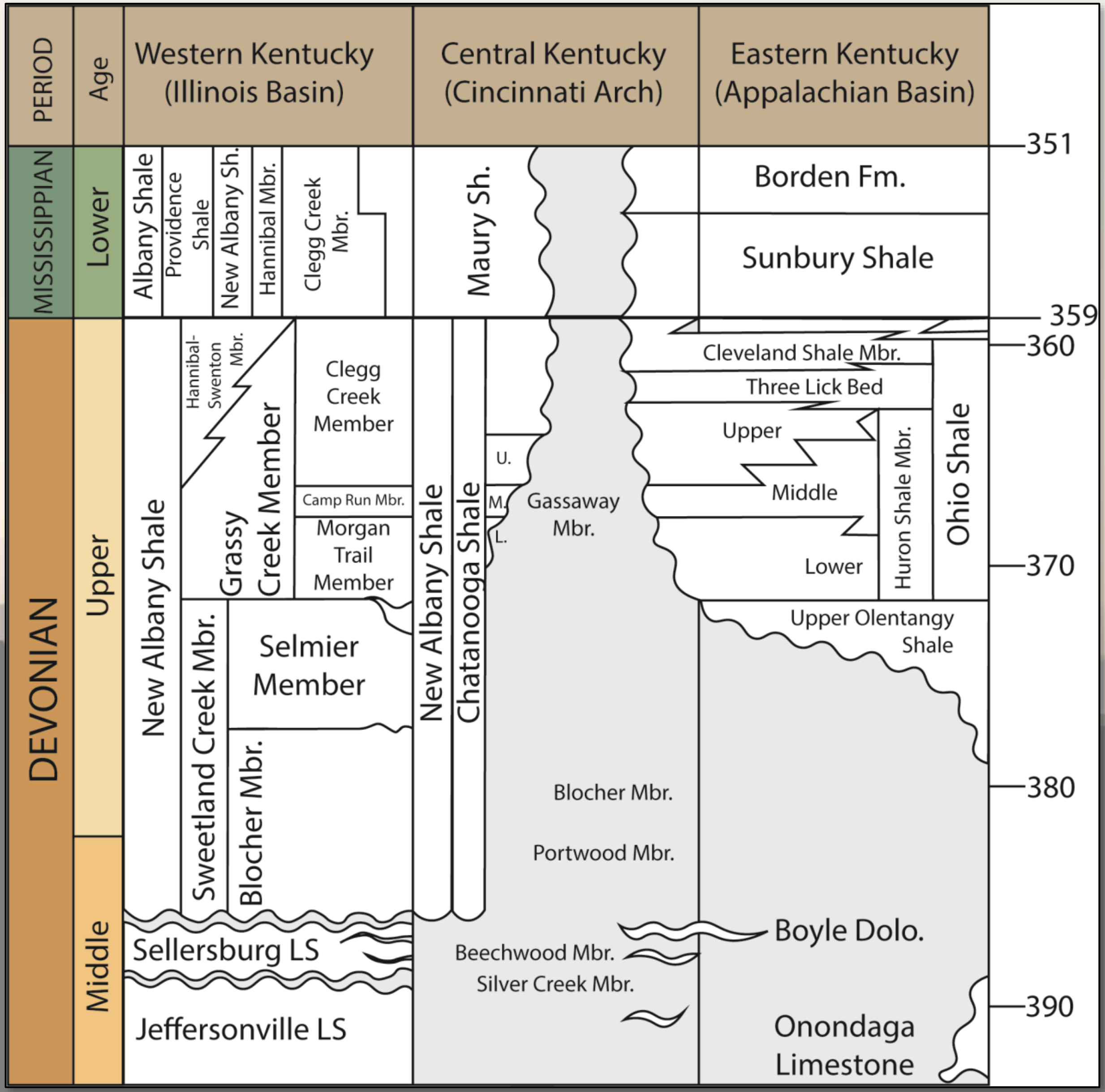
- **Purpose**: Devonian shales of Kentucky are being investigated for trace and rare earth elements as a potential source of critical elements
- **Hypothesis**: High enrichment of trace metals in Devonian shales of Kentucky are the result of bottom-water anoxia and the deposition and preservation of organic matter

Geologic Background

- Kentucky hosts the intersection of the Appalachian and Illinois Basins across the Cumberland Saddle
- Structure defined by rise of Cincinnati Arch, with later deformation from tectonics of the Alleghanian Orogeny



Geologic Background

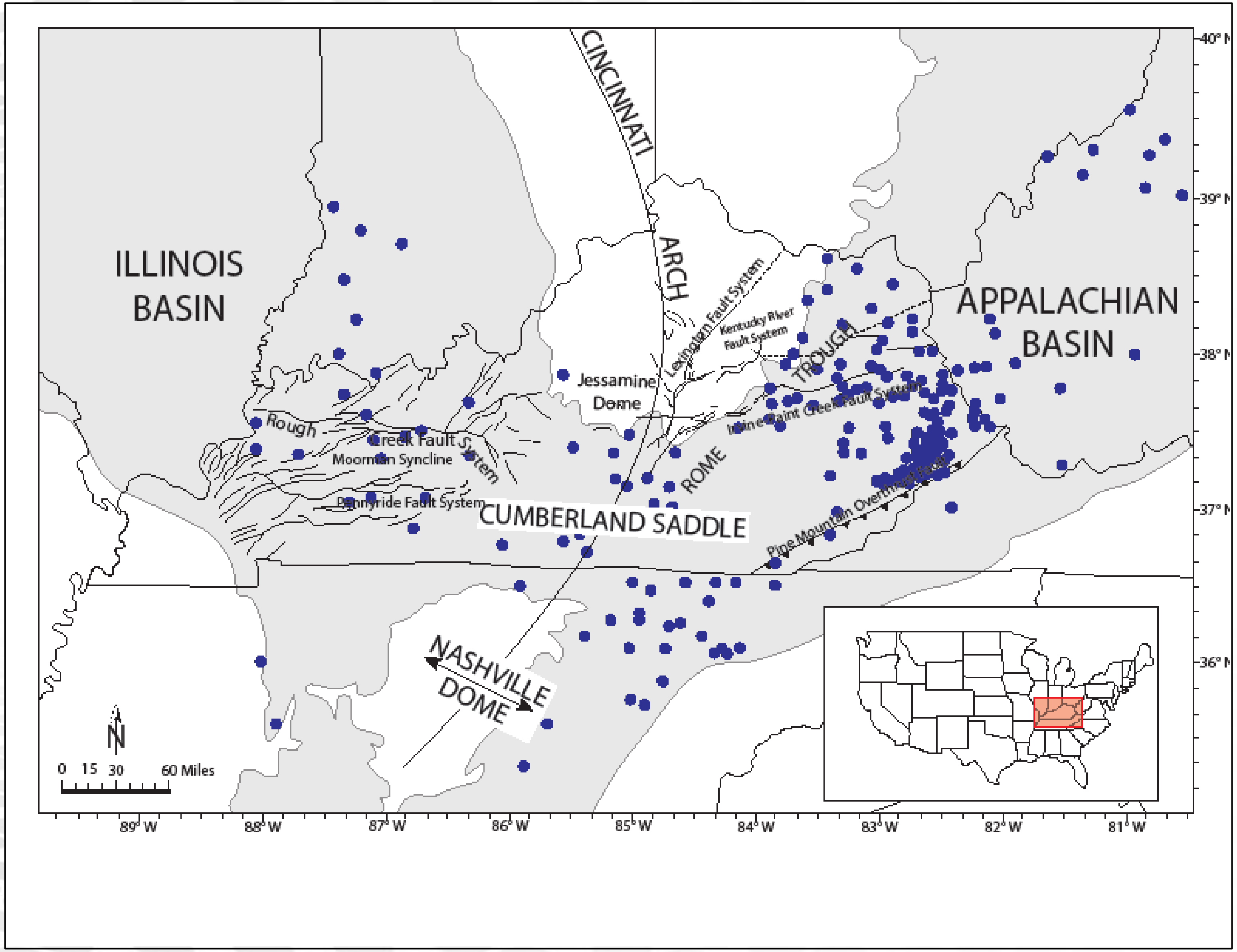


- Deposition of shales limited mostly to the Upper Devonian in Kentucky
- Primary units are the Ohio, Chatanooga, and New Albany shales
- Previously explored for uranium enrichment and petroleum resources

Methods

Samples:

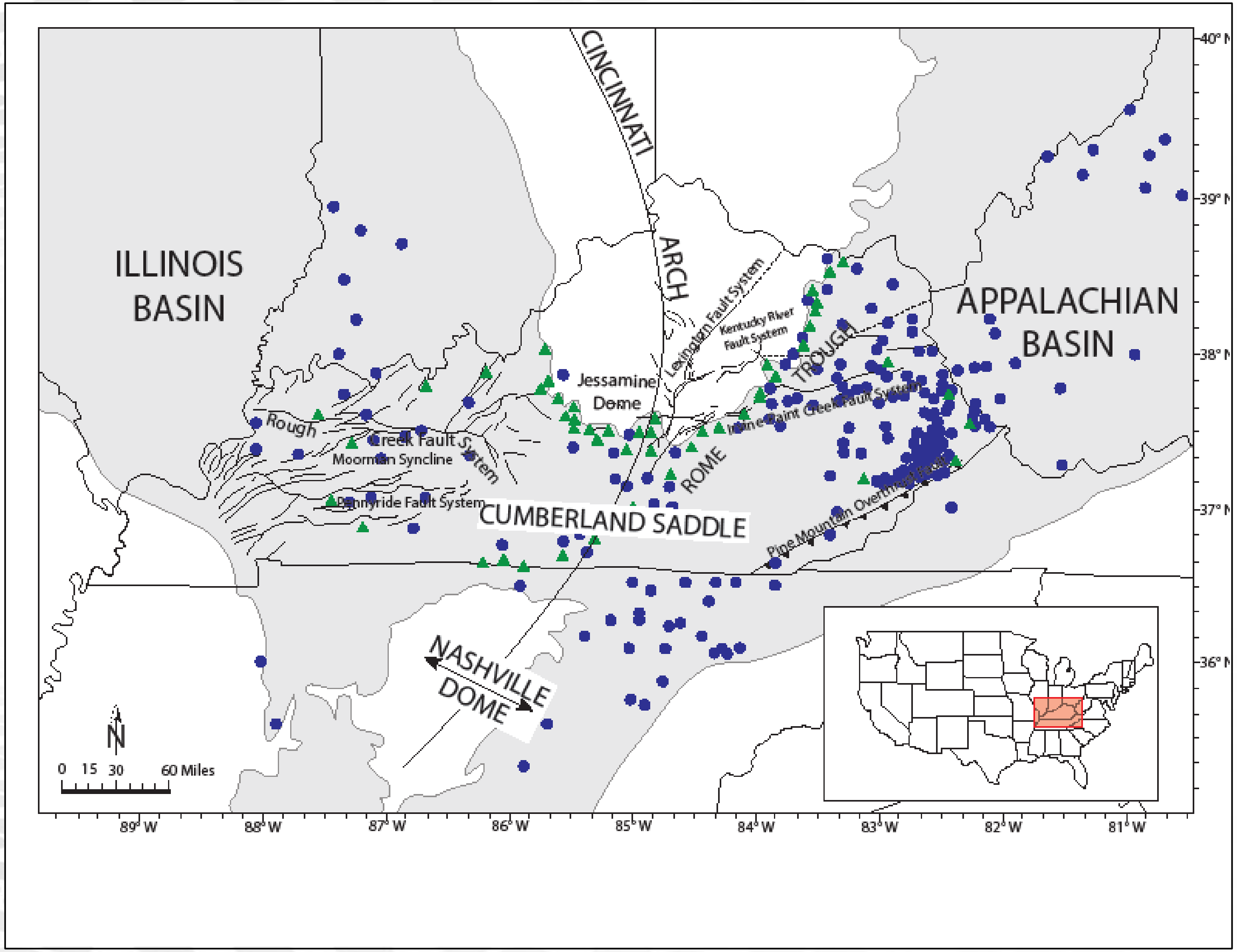
1. 298 Wells with Electric Logs



Methods

Samples:

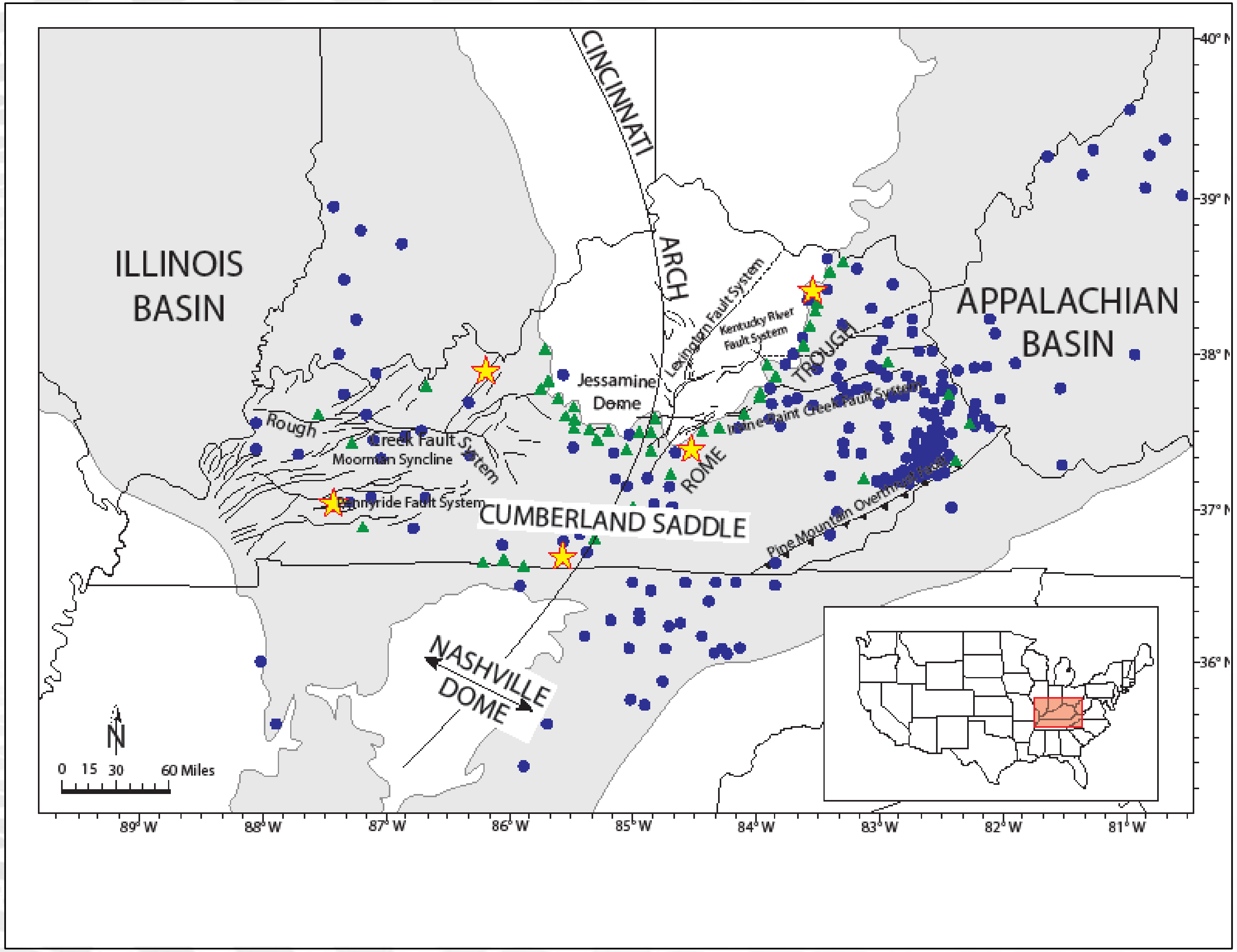
1. 298 Wells with Electric Logs
2. 77 wells cored through the Devonian interval



Methods

Samples:

1. 298 Wells with Electric Logs
2. 77 wells cored through the Devonian interval
3. 112 samples from 5 wells taken for geochemical and mineralogical analysis



Methods

Samples:

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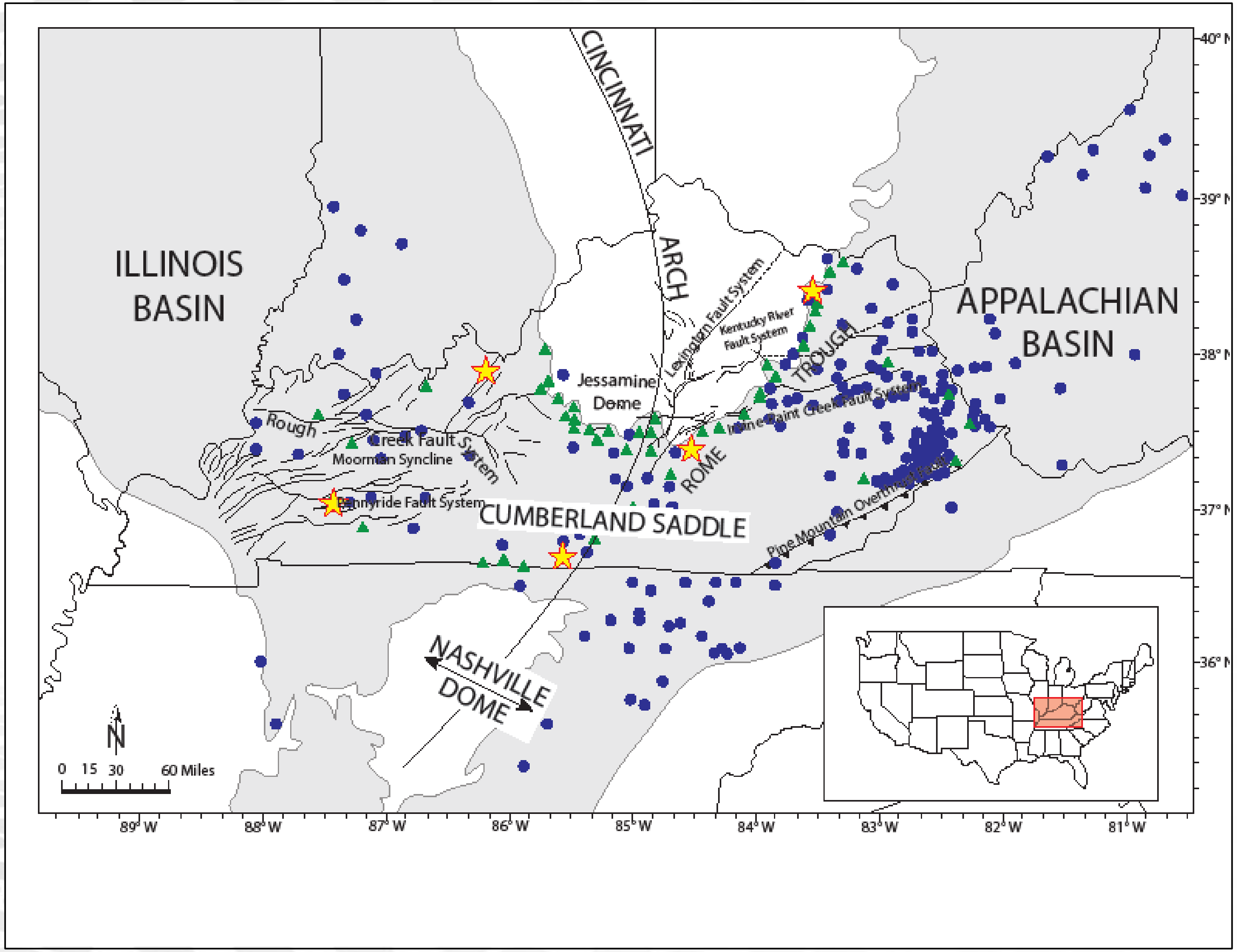
3. 112 samples from 5 wells taken for geochemical and mineralogical analysis
4. Additional 42 samples from the same 5 wells for other geochemistry



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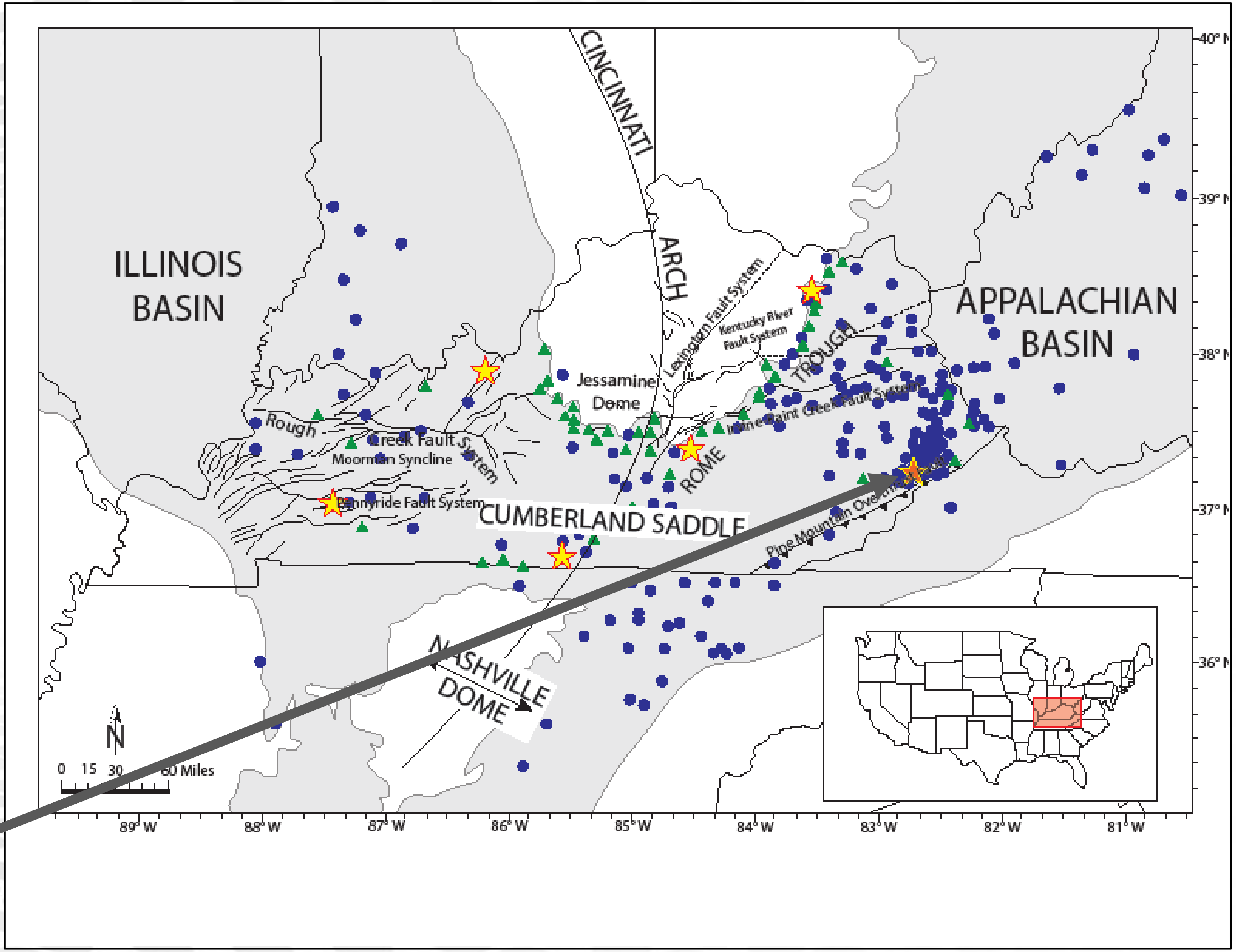
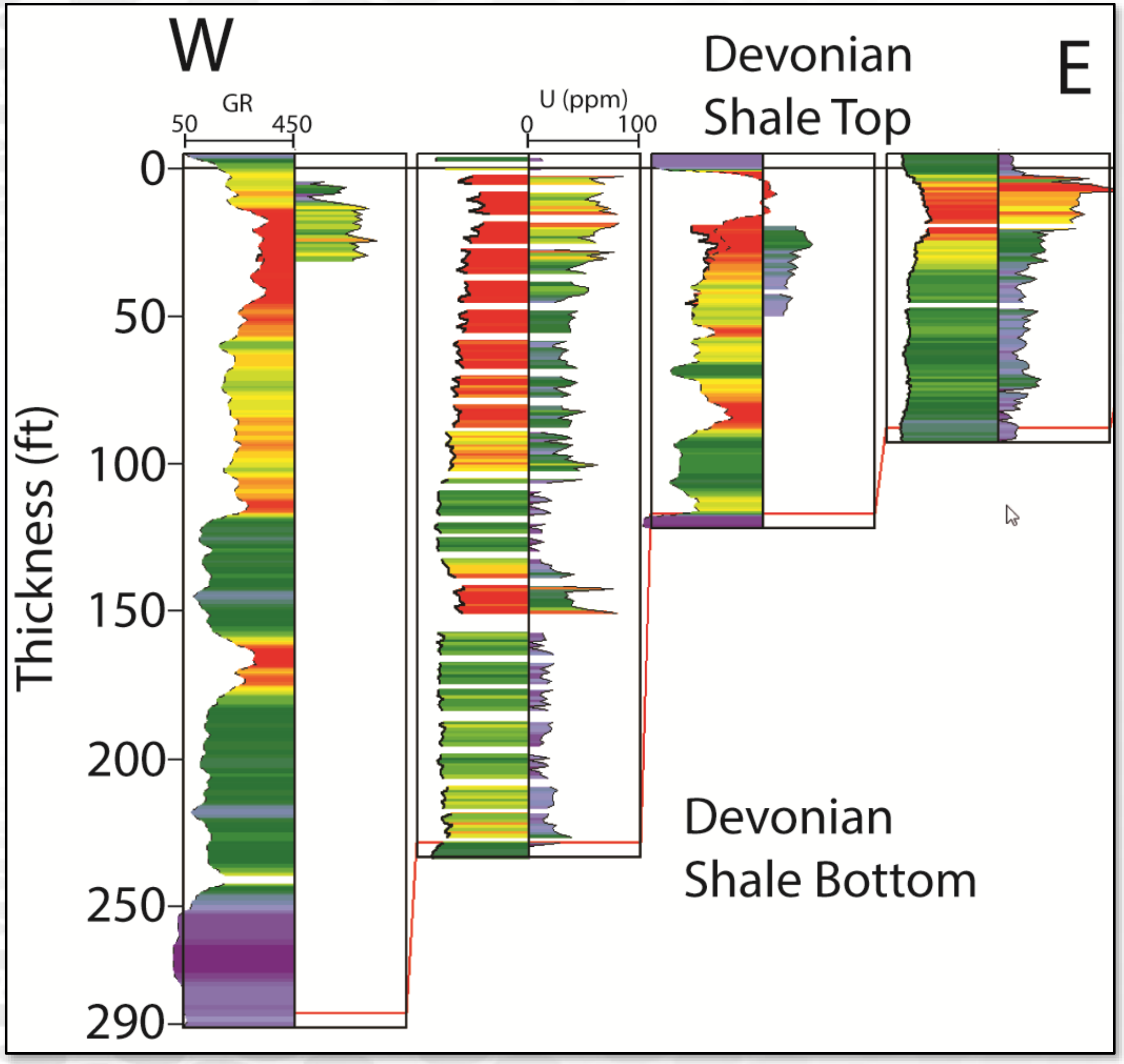
5. Comparison to previous work by Abshire et al., (2022)



Methods

Analyses:

1. Stratigraphic correlations by electric well logs



Methods

Analyses:

1. Stratigraphic correlations by electric well logs
2. Element geochemistry by pXRF and handheld gamma-ray (GR) on all core
   - 1' sampling interval
   - Direct analysis on fresh surfaces
   - Mudstone factory calibration
   - 60s low energy and 60s high energy analyses

Bruker Tracer 5 pXRF

Super Spec RS-125 Scintillometer

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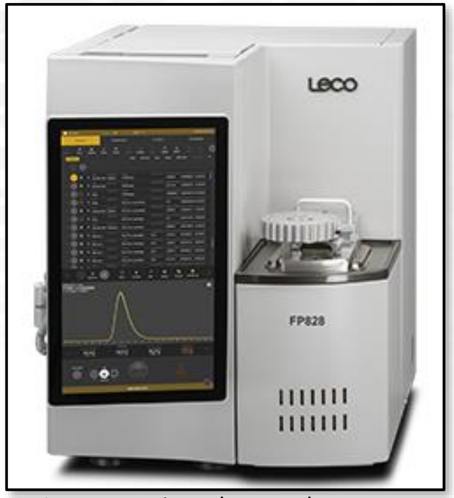
3. Geochemistry on 112 samples
   - TC+IC+TOC Analysis
   - ICP-MS for trace and rare earth elements (in process)
   - Mineralogy via XRD (in process)

coulometer



Leco organic carbon analyzer

Quadrupole mass spectrometer

Bruker Advance 8 X-Ray Diffractometer

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   - Mineralogy via XRD (in process)
4. U-Isotope Analysis on 42 samples (in process)
   - Identification of U source (e.g. marine water, hydrothermal, etc.)

Quadrupole at the Arizona State University METALS lab

Validation - Correlations

How accurate are the pXRF results?

- WD-XRF vs. pXRF

Oxides

	SiO2	Al2O3	CaO	MgO	F2O3	K2O	Na2O	TiO2	P2O5
Correlation Coefficient	0.19	0.35	0.14	0.45	0.38	0.38	0.09	0.48	-0.05
R2	0.04	0.12	0.02	0.21	0.15	0.15	0.01	0.23	0.00

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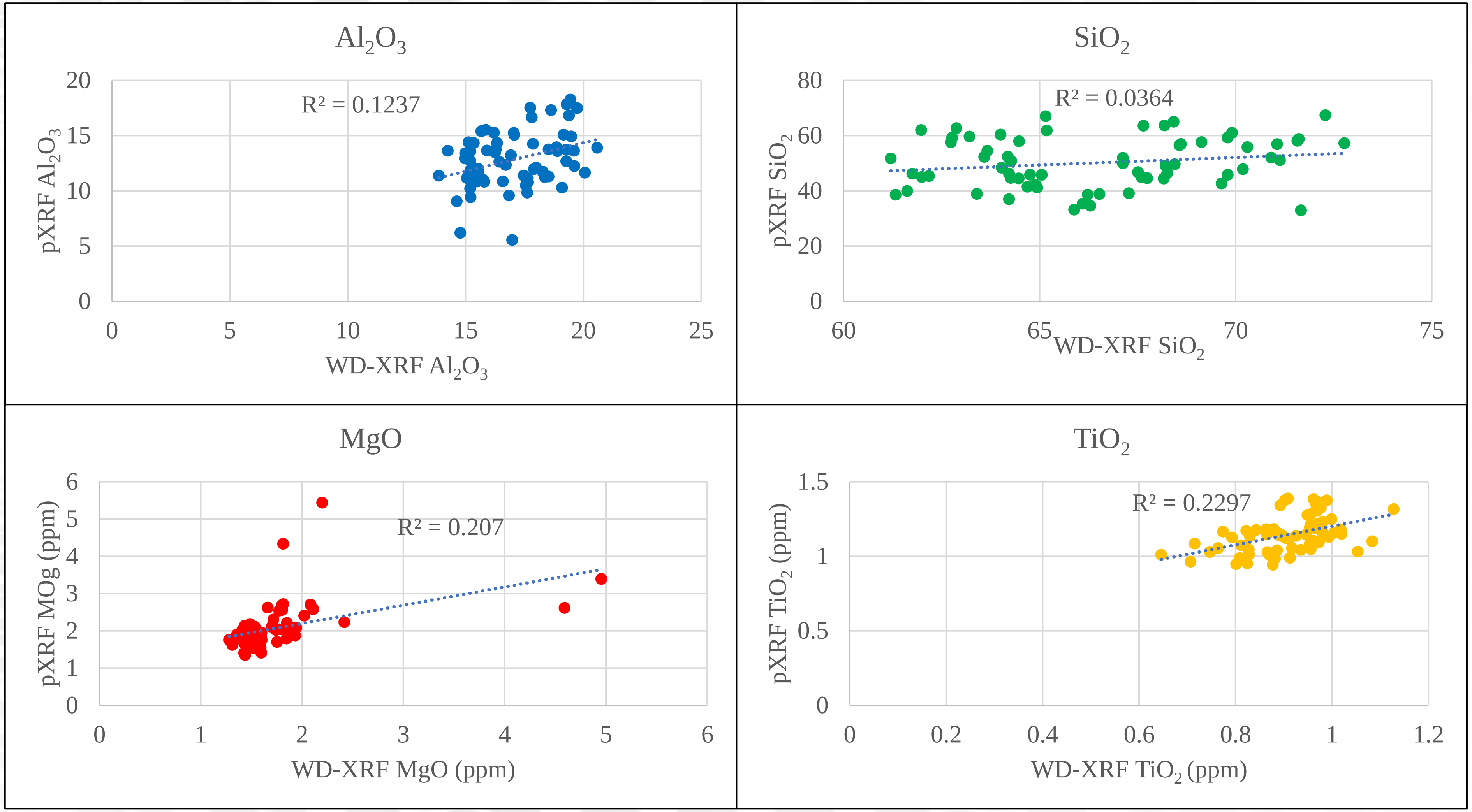

Validation - Correlations

How accurate are the pXRF results?

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Trace Metals

	Ba	Co	Cr	Cu	Mo	Ni	Sr	Th	U	V	Zn	Zr
Correlation Coefficient	0.09	0.18	0.77	0.58	0.88	0.80	0.49	0.29	0.83	0.91	0.68	0.65
R2	0.01	0.03	0.60	0.33	0.77	0.63	0.24	0.08	0.69	0.83	0.46	0.42

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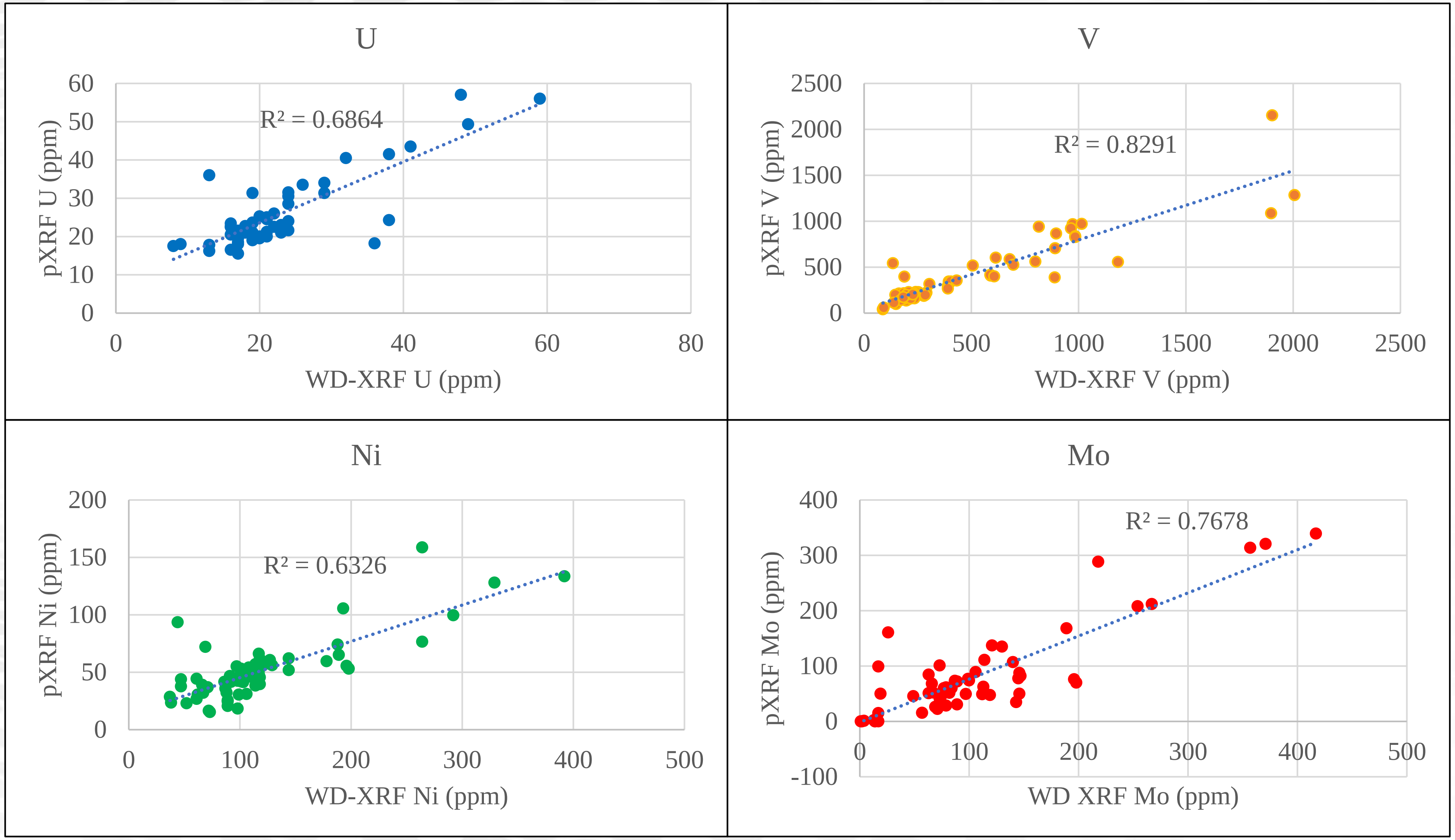
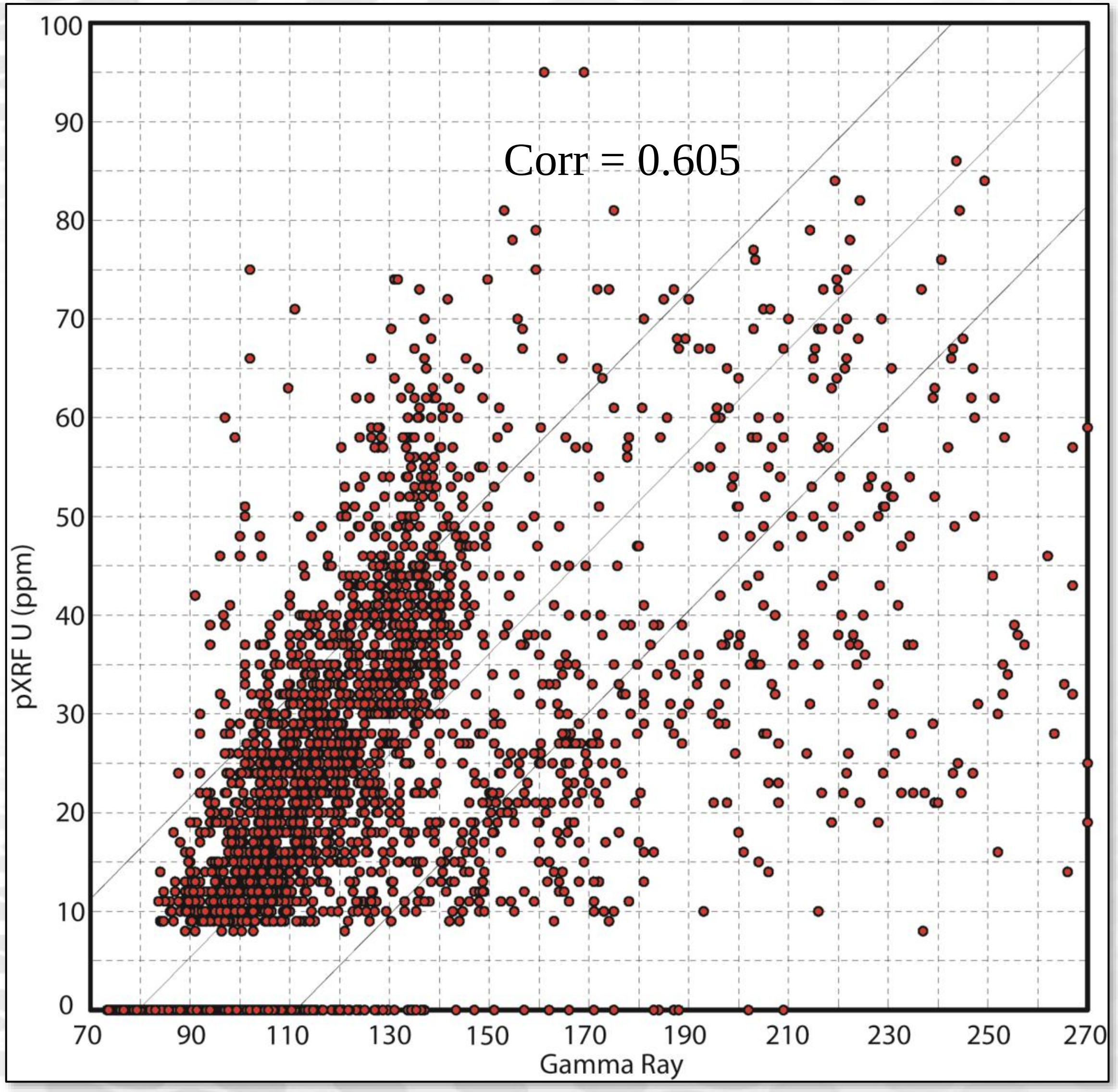


Validation - Correlations

How accurate are the pXRF results?

- WD-XRF vs. pXRF
- GR vs. U (ppm)

All Cored Wells



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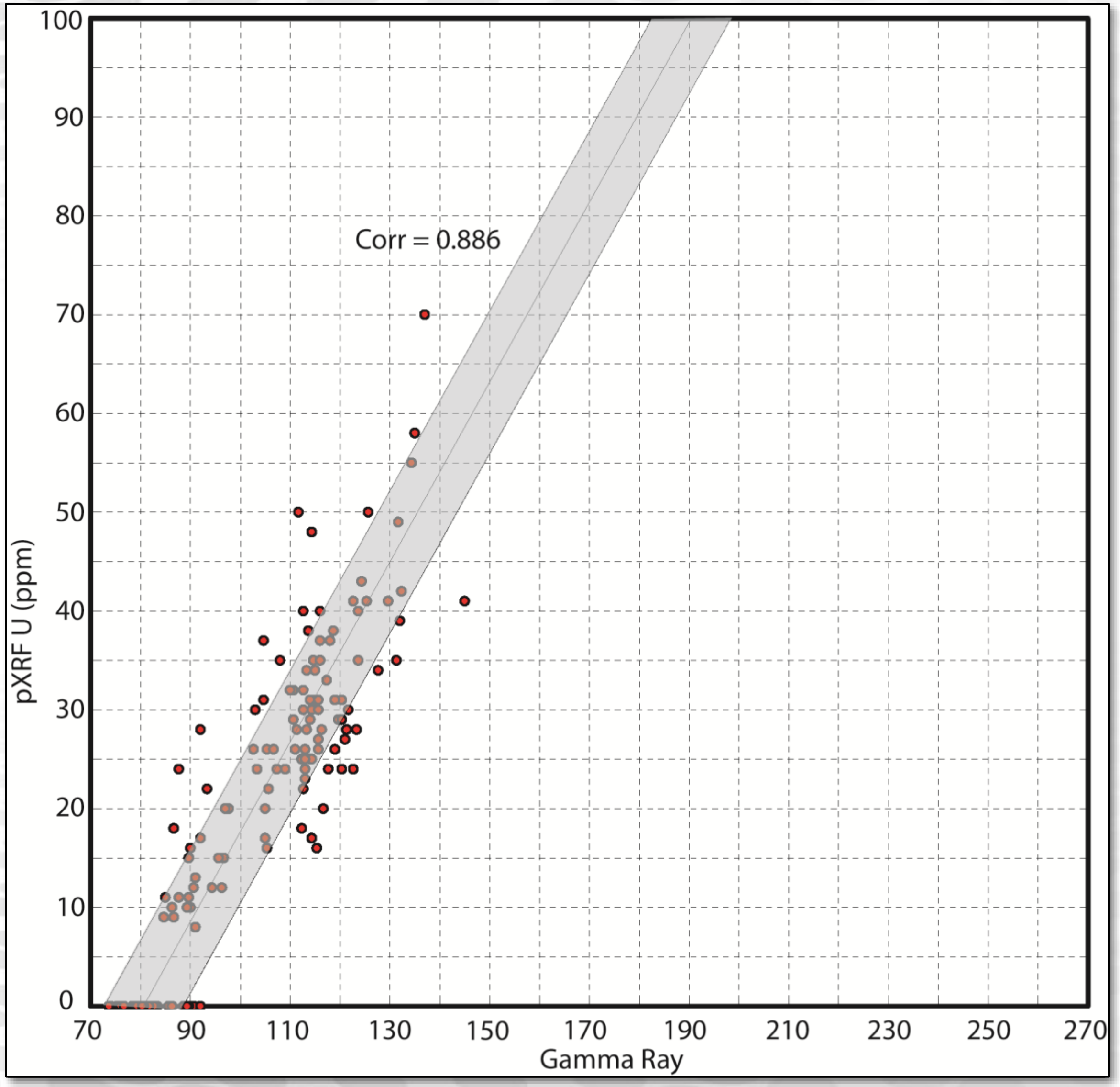

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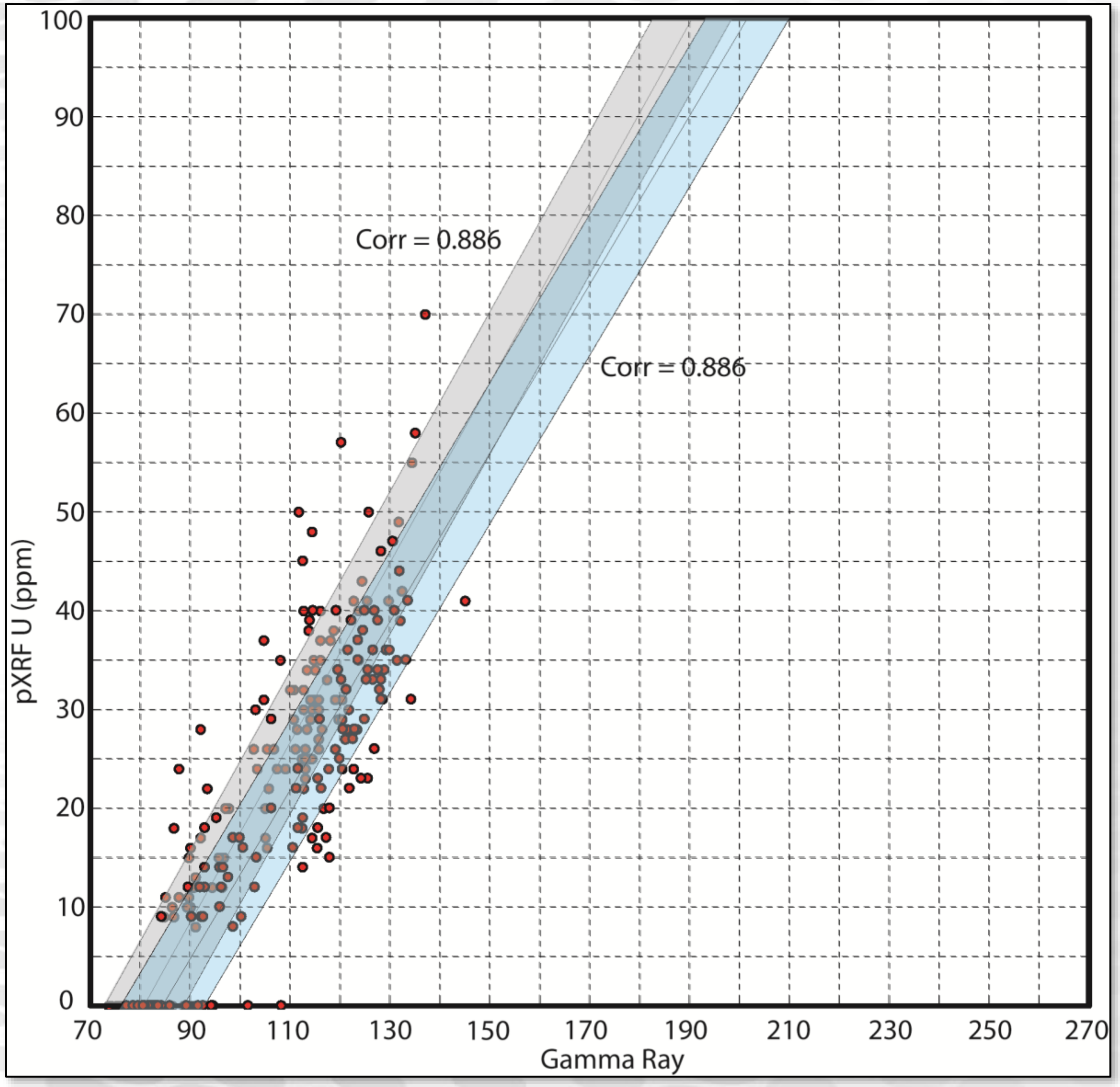

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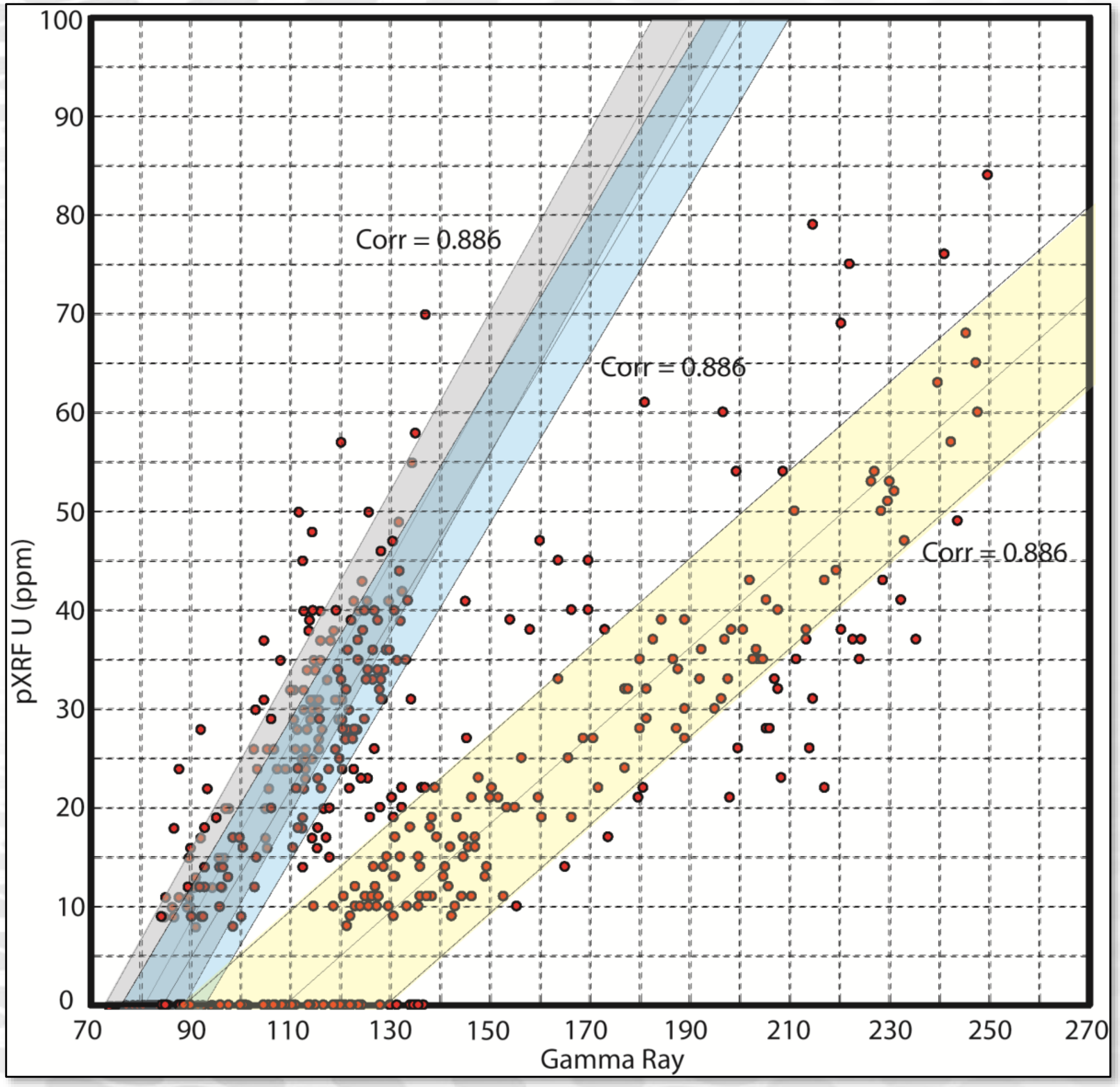
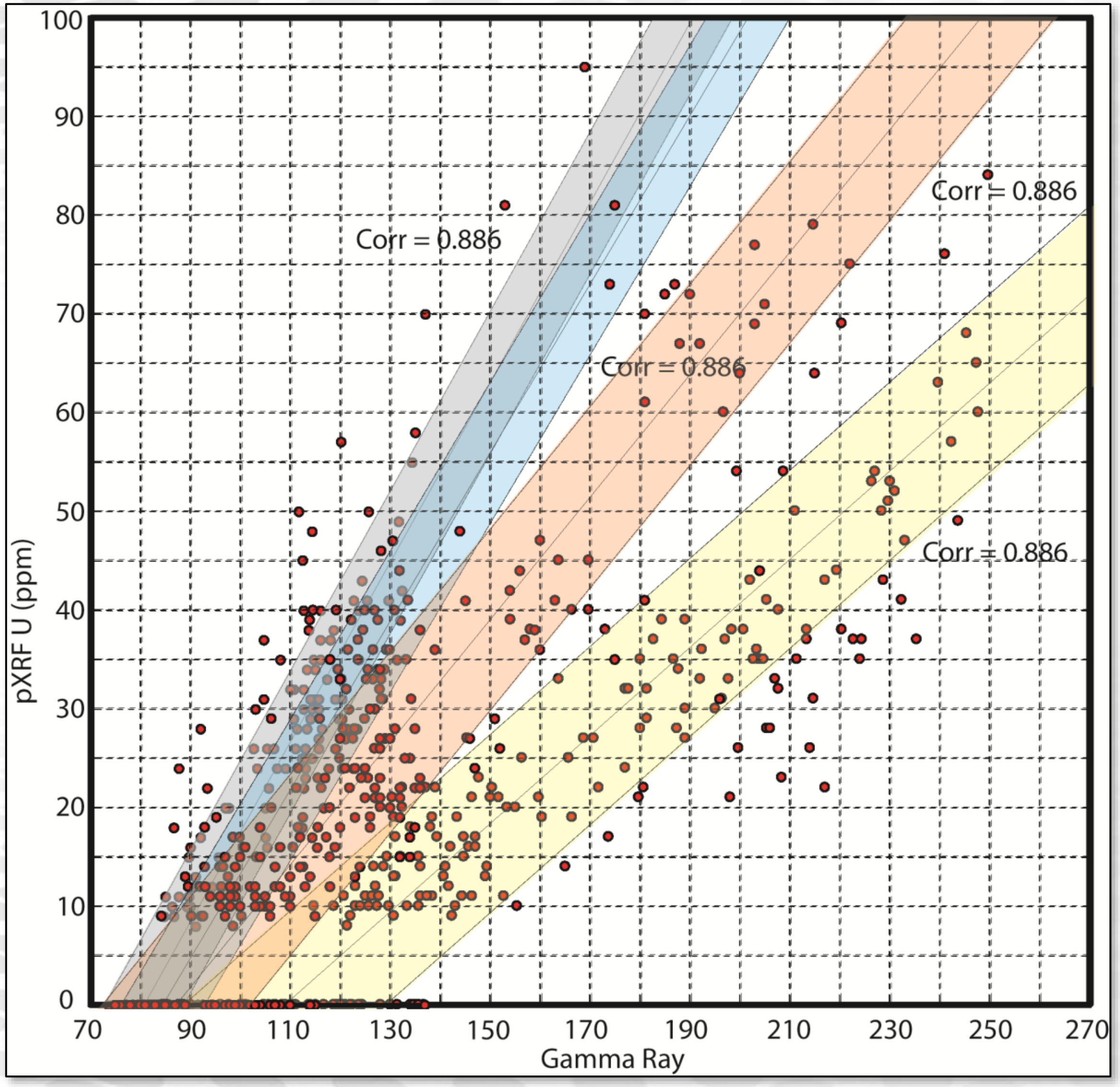


Validation - Correlations

How accurate are the pXRF results?

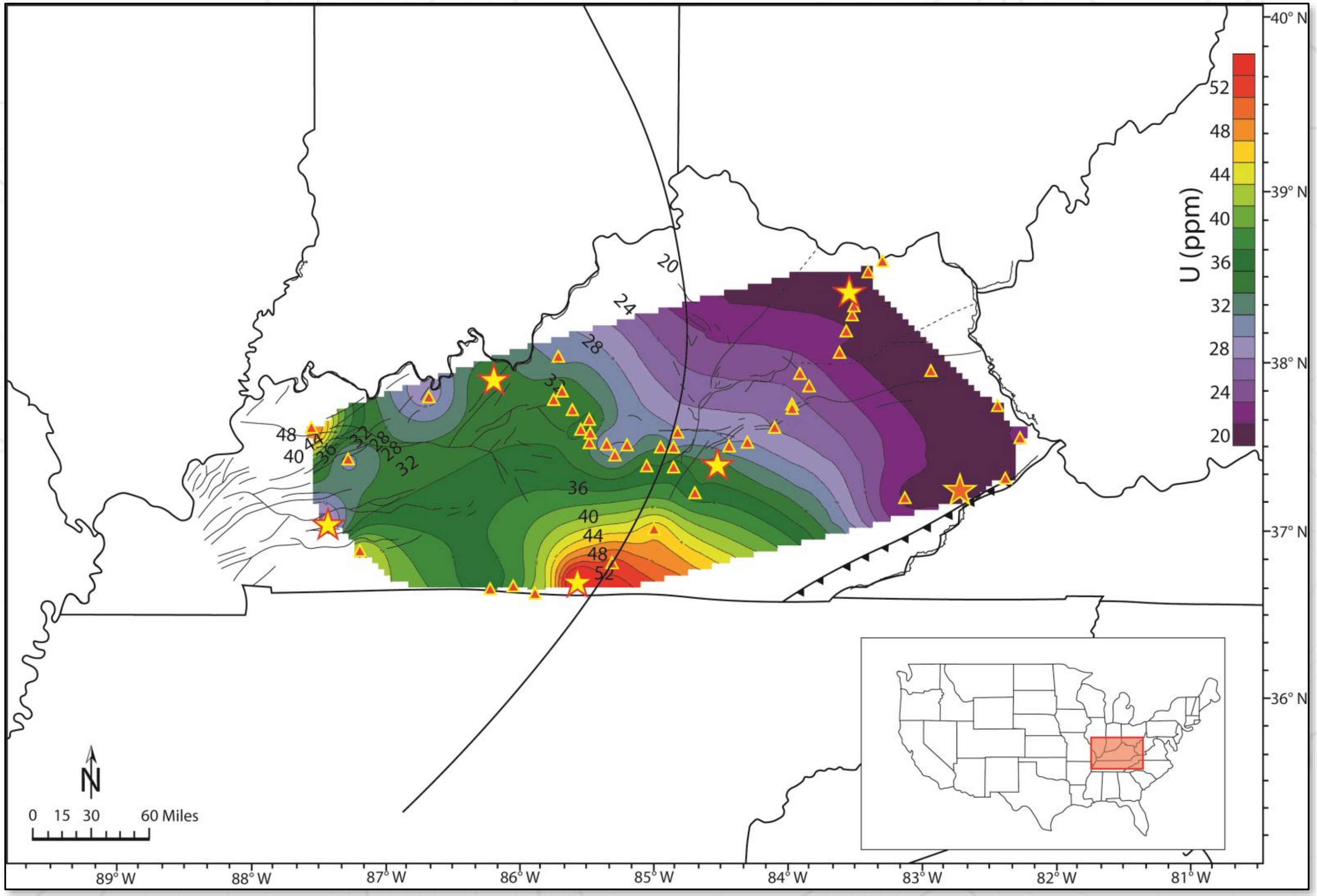
- WD-XRF vs. pXRF
- GR vs. U (ppm)

Conclusion: GR is usable as a proxy for U and other redox-sensitive trace elements in Devonian shales of Kentucky, *but only after GR curve normalization*



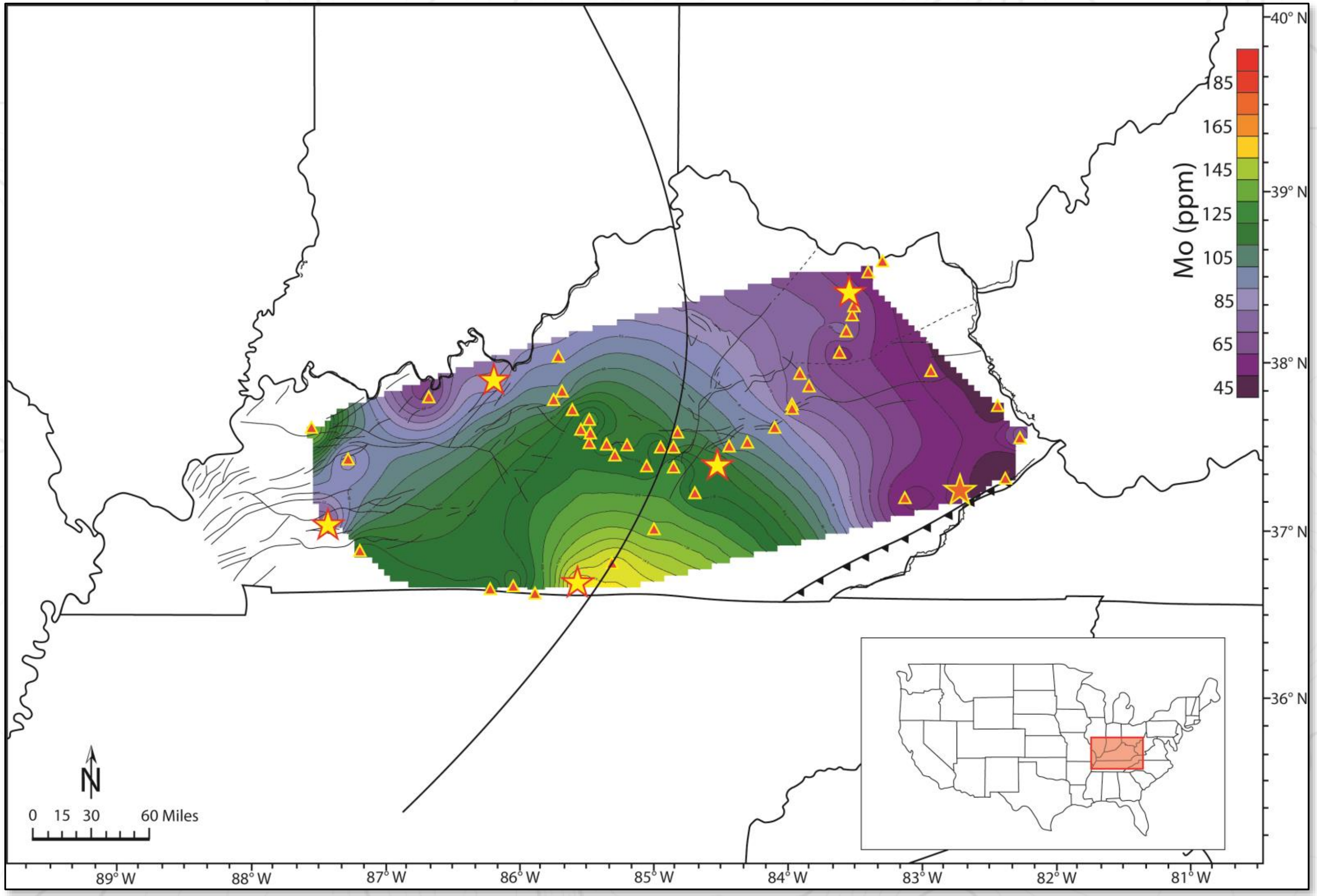
Spatial Element Distribution

- Average U in Devonian black shales
- Clear trend from NE to SW
- U is highly enriched (3-20x vs. average shales)



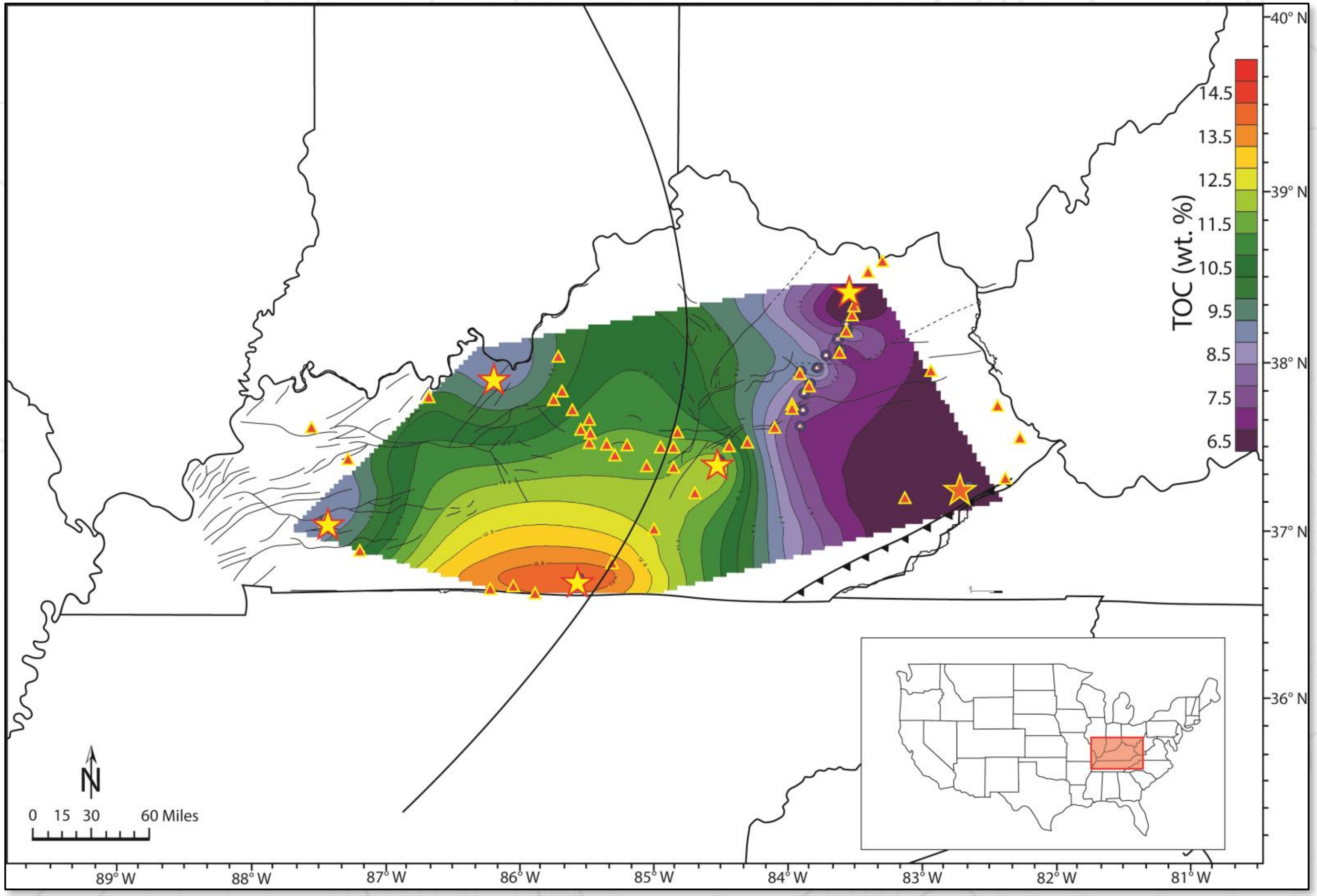
Spatial Element Distribution

- Similar trend from NE to SW in all redox-sensitive metals (Cr, V, etc)
- Mo is highly enriched (35-145x vs. average shales)
- **QUESTION:** *What is controlling the enrichment of metals?*



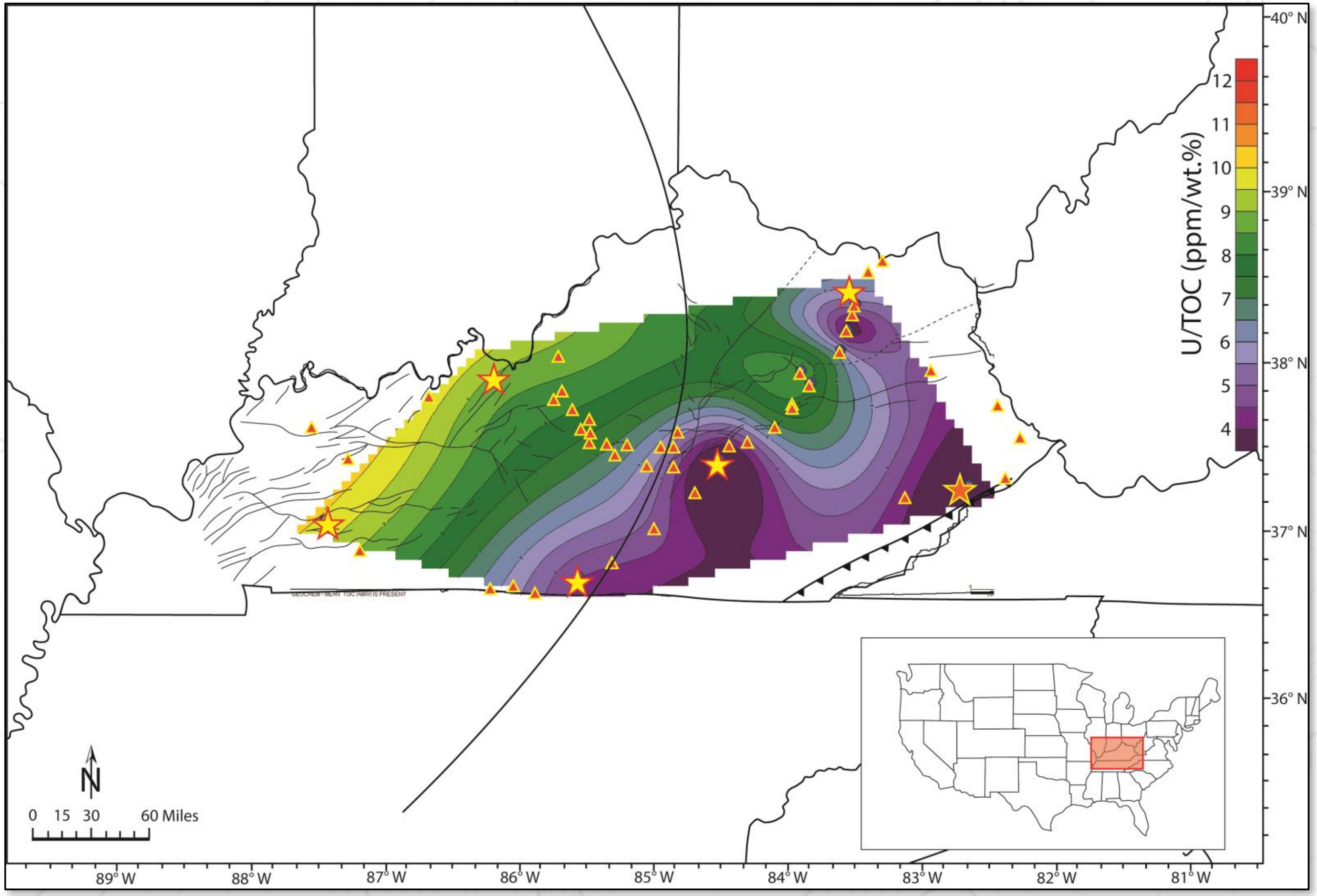
Spatial Element Distribution

- Similar trend from NE to SW for Total Organic Carbon (TOC)
- Suggests metal enrichment from high organic matter deposition/preservation



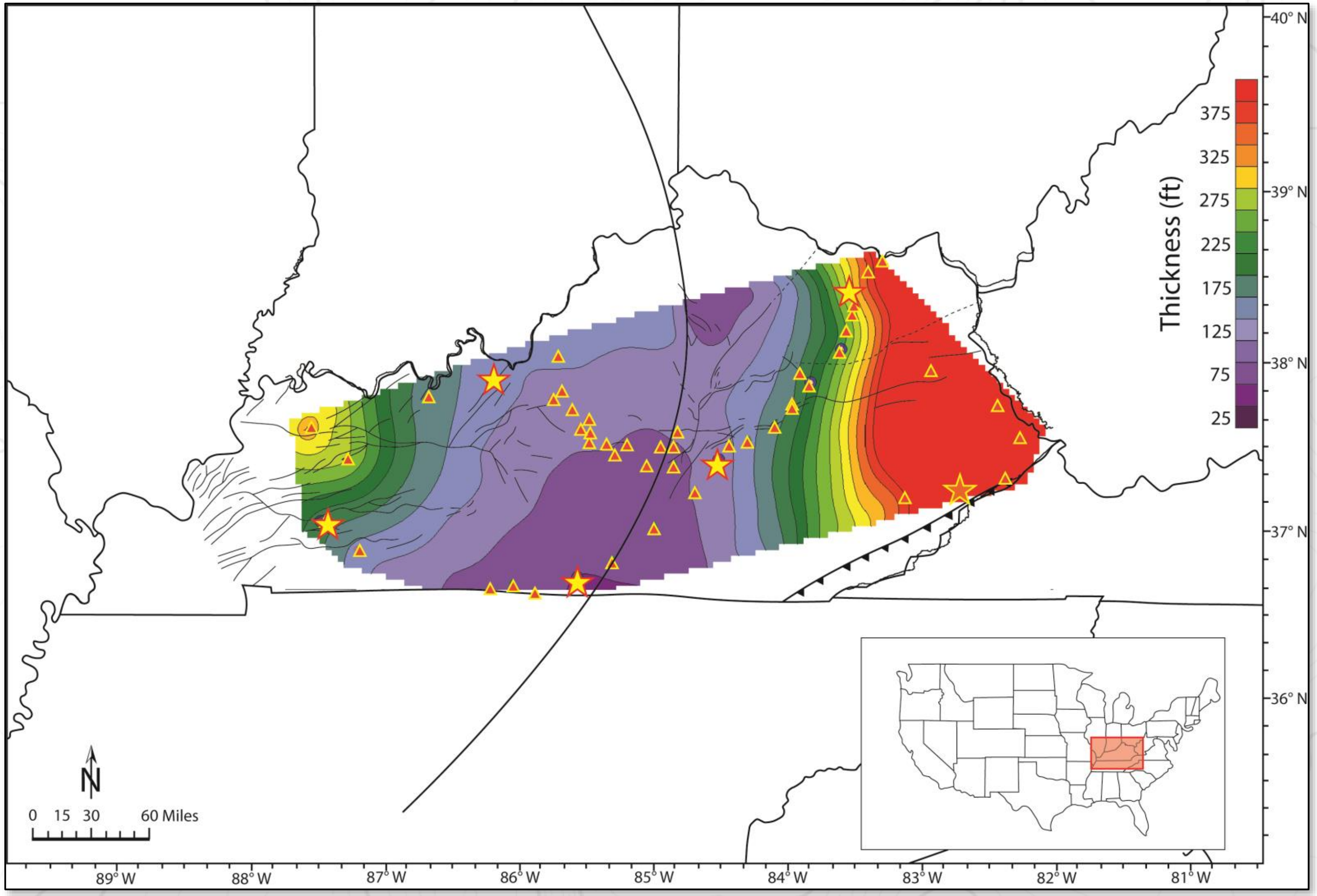
Spatial Element Distribution

- Relatively consistent trend of U/TOC from NE to SW supports U associated with organic matter
- Elevated U/TOC moving west

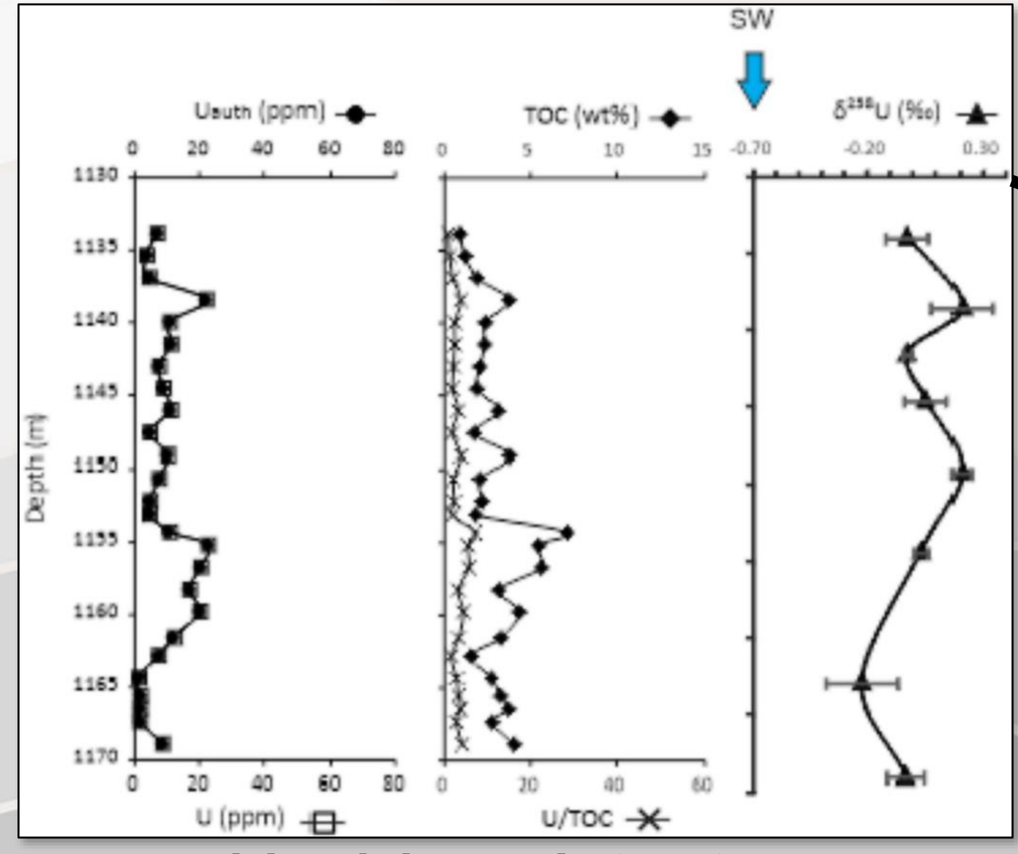


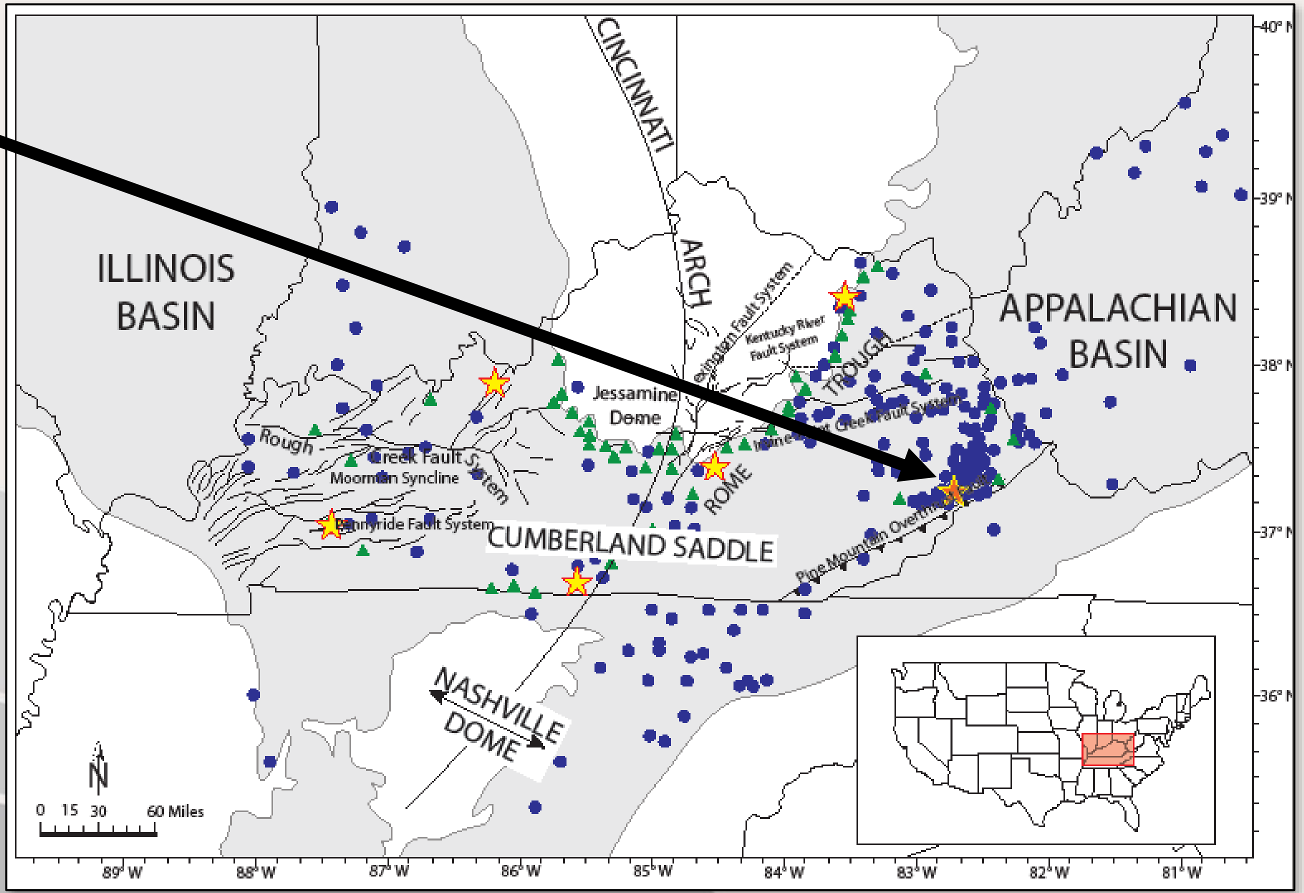
Spatial Element Distribution

- Lower TOC and metal enrichment in thicker portion of Appalachian Basin
- Organic matter preservation driven by high productivity/water column stratification outpacing oxygen replenishment, not rapid sedimentation



Connecting Spatial & Temporal Changes





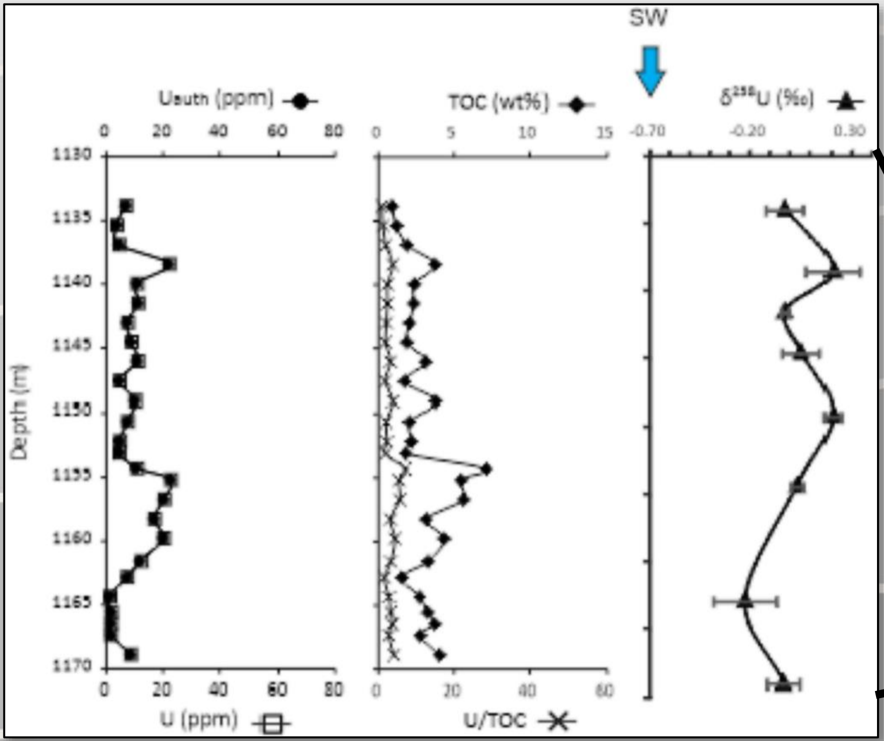
Previous work by Abshire et al., (2022) using U-isotopes in Cleveland Shale

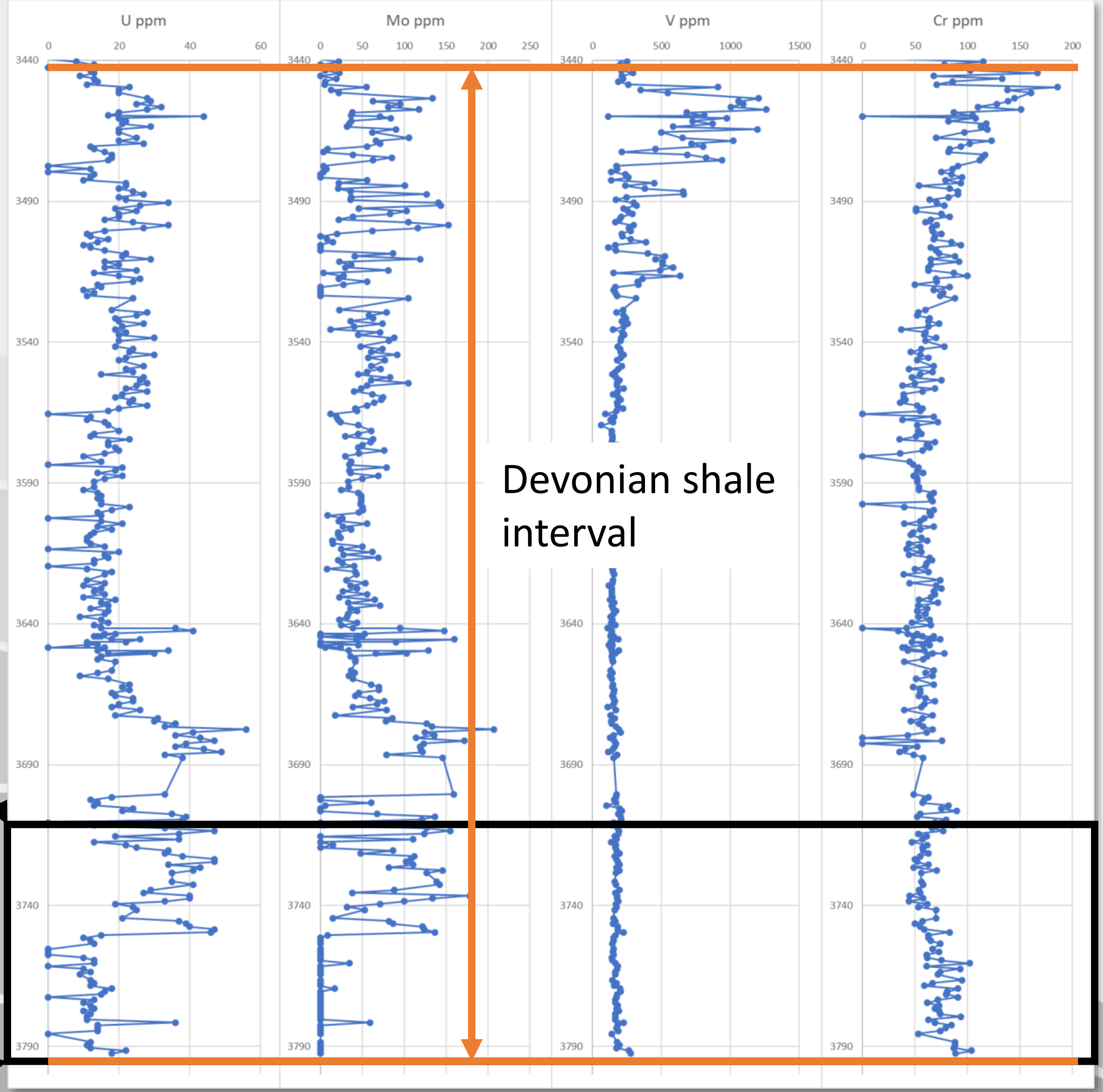
- Low U/TOC ratio (~3)
- $\delta^{238}U$ ranged from -0.22 to 0.21
- *Fluctuating pycnocline* and *changing redox conditions* along basin margin responsible for anoxia and subsequent U enrichment

Connecting Spatial & Temporal Changes

Previous work by Abshire et al., (2022) using U-isotopes in Cleveland Shale

- Small portion of Devonian shale interval
- Only one well analyzed





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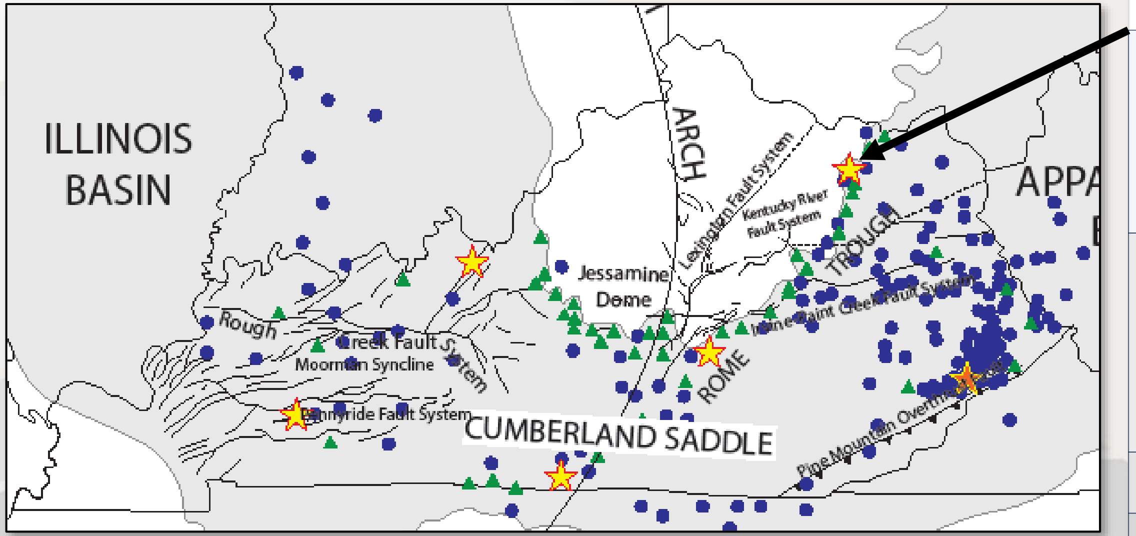
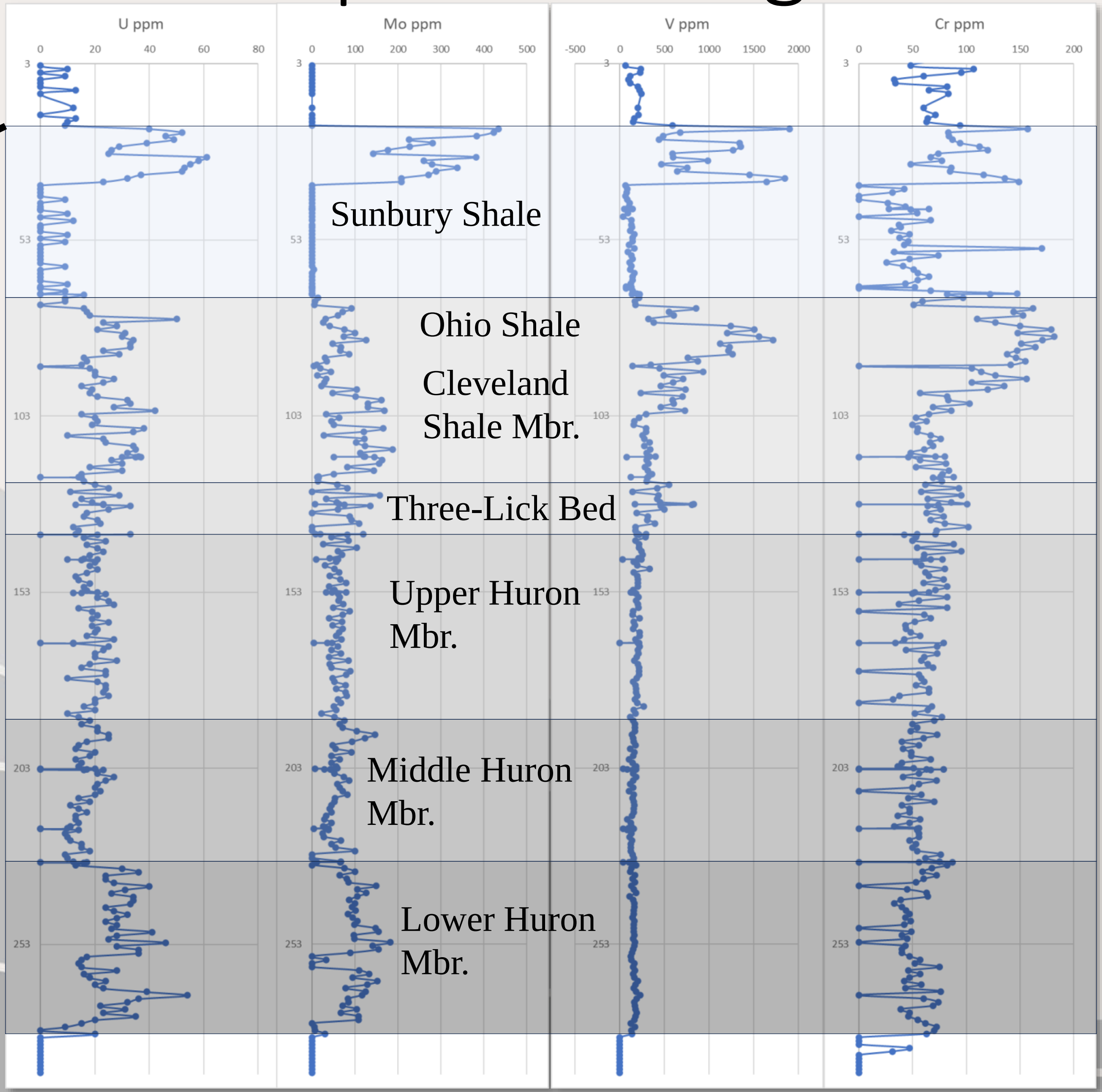
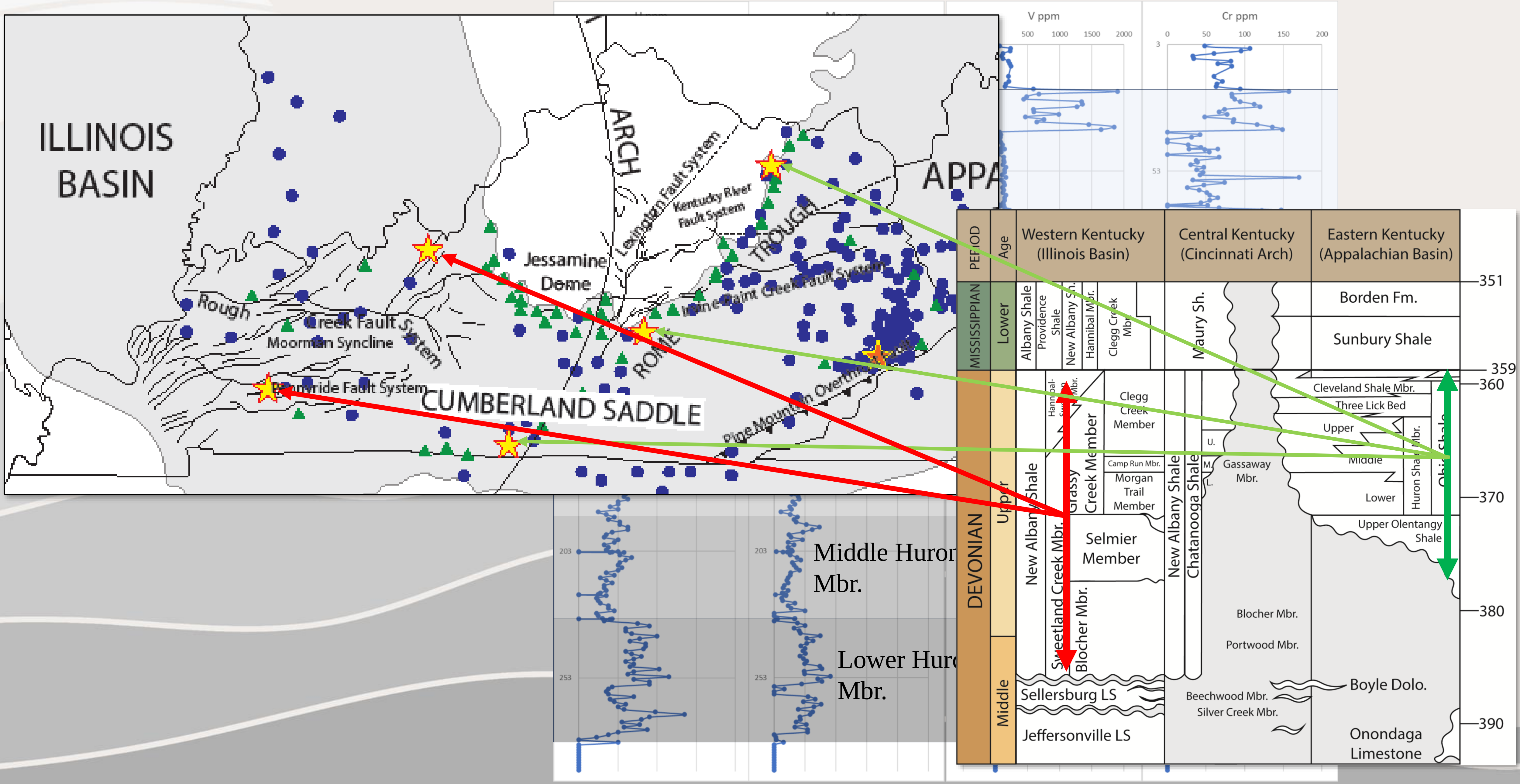




- pXRF results from northernmost well
- Significant variability in redox-sensitive elements across various members

Connecting Spatial & Temporal Changes

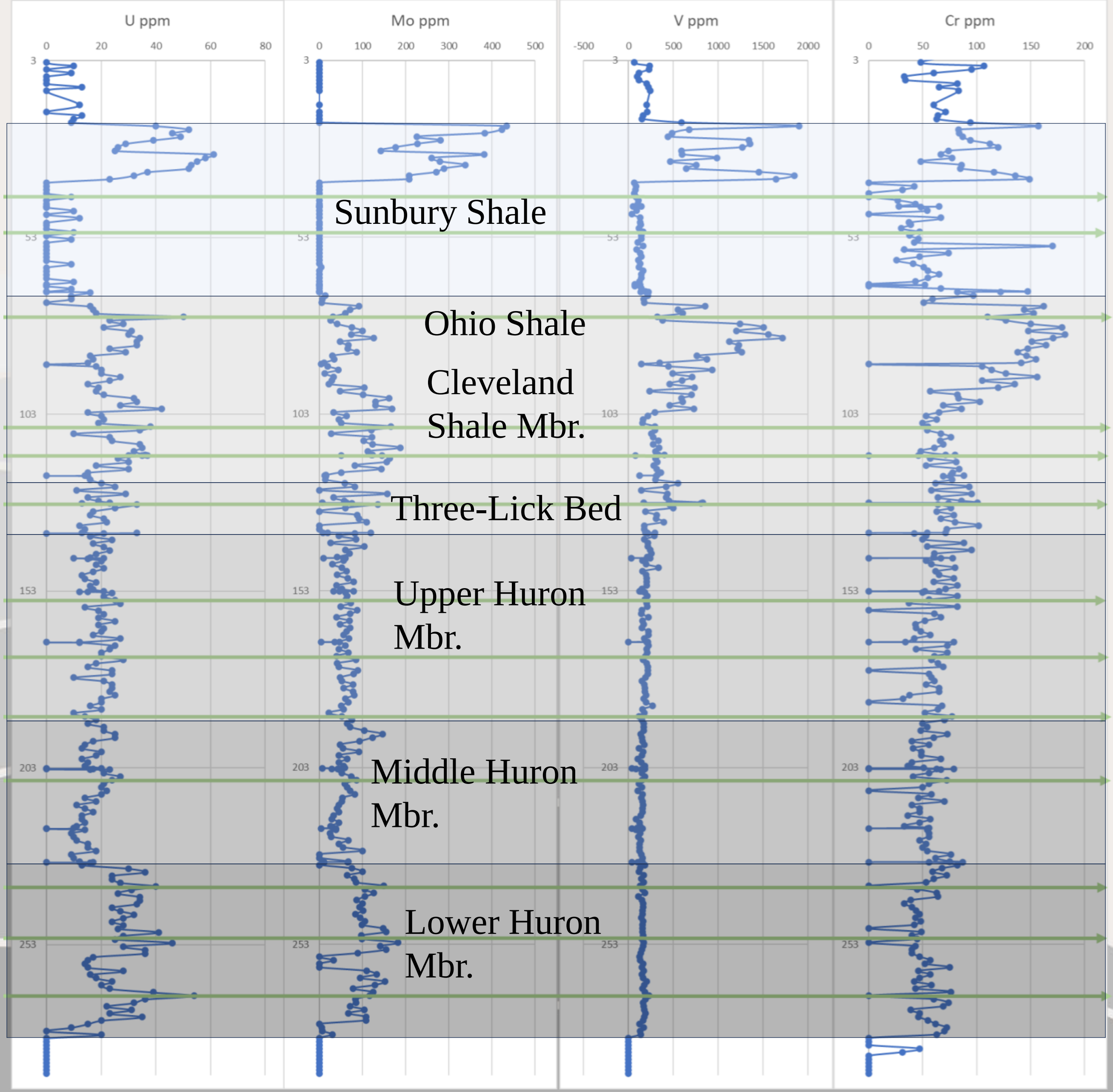


Connecting Spatial & Temporal Changes

- Planned analyses of:

1. U-isotopes to determine source of authigenic U
2. ICP-MS trace and rare-earth element geochemistry
3. XRD mineralogy

- Analyses in progress
- **Purpose:** Identify spatial and temporal changes in anoxia and U source



Conclusions

Spatial trends in TOC, redox-sensitive element abundance, and thickness correlate

GR may be used as proxy for U and other redox-sensitive elements in Devonian shales of Kentucky

Metal enrichment in Devonian black shales caused by anoxia and facilitated by deposition and preservation of organic matter

Causes of anoxia are topic of ongoing investigation


Questions