

Trace Metal Geochemistry and Mobility in the Marcellus Shale

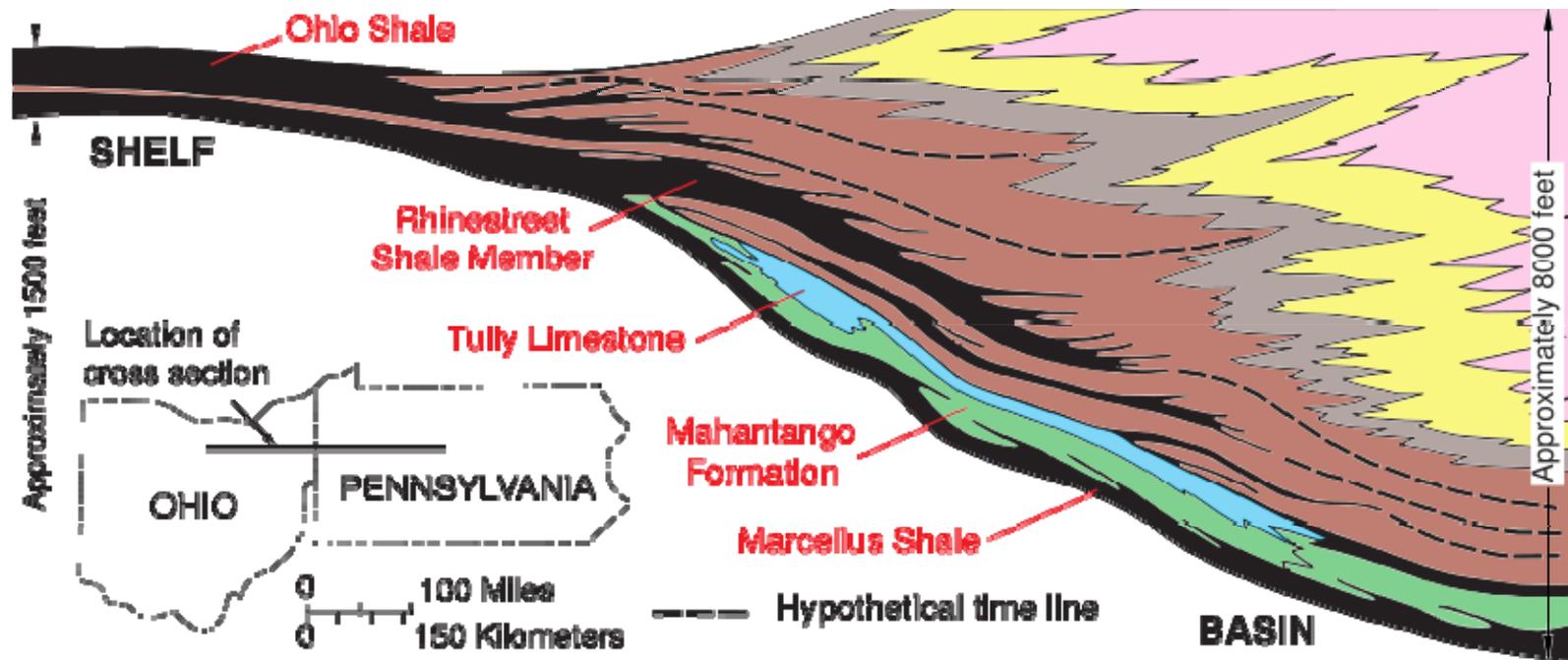
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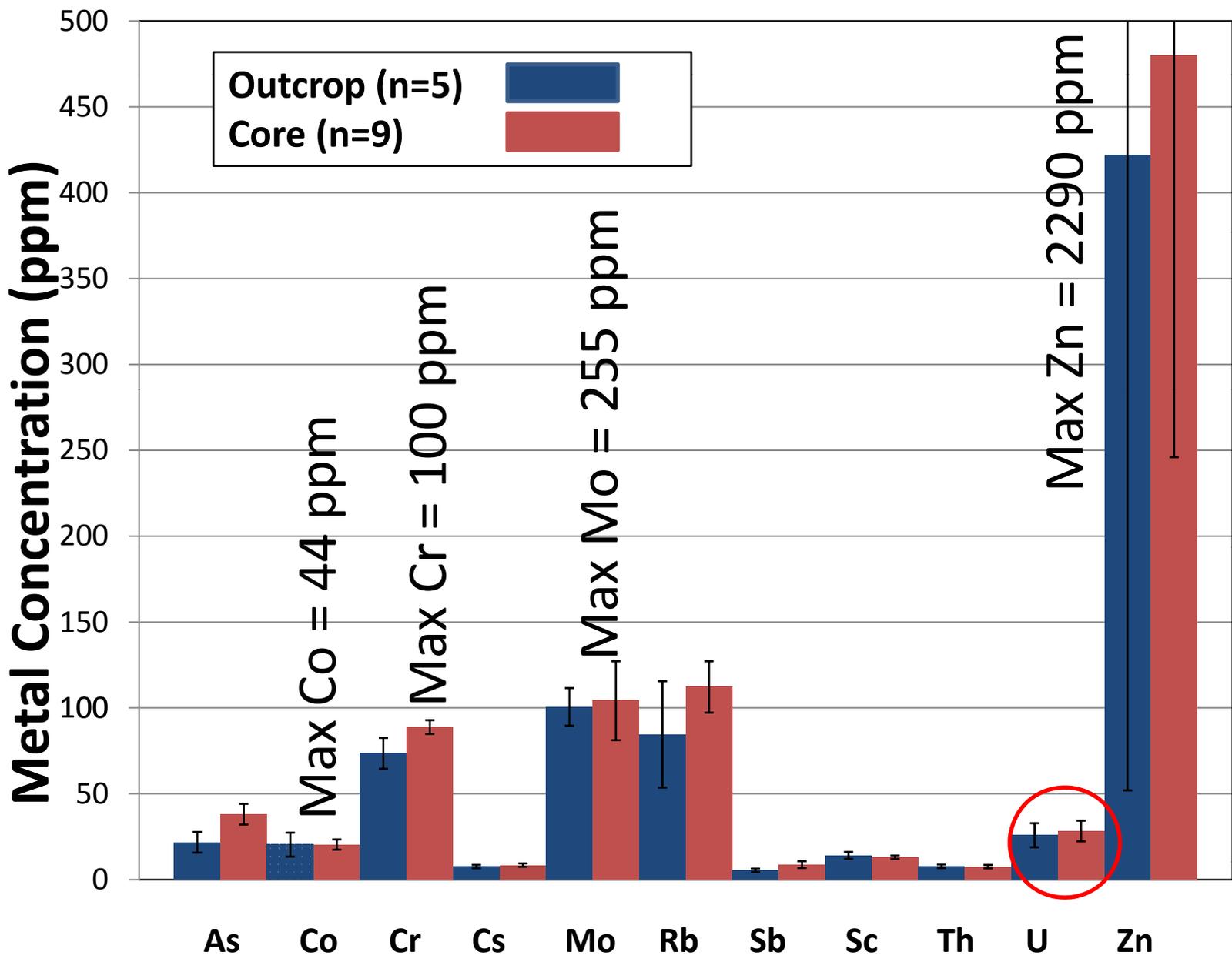
Marcellus Shale Samples

- 22 samples including core, outcrop and well cuttings
- All samples from NY and northern PA
- 16 core and outcrop samples analyzed



Shale Mineralogy & Geochemistry

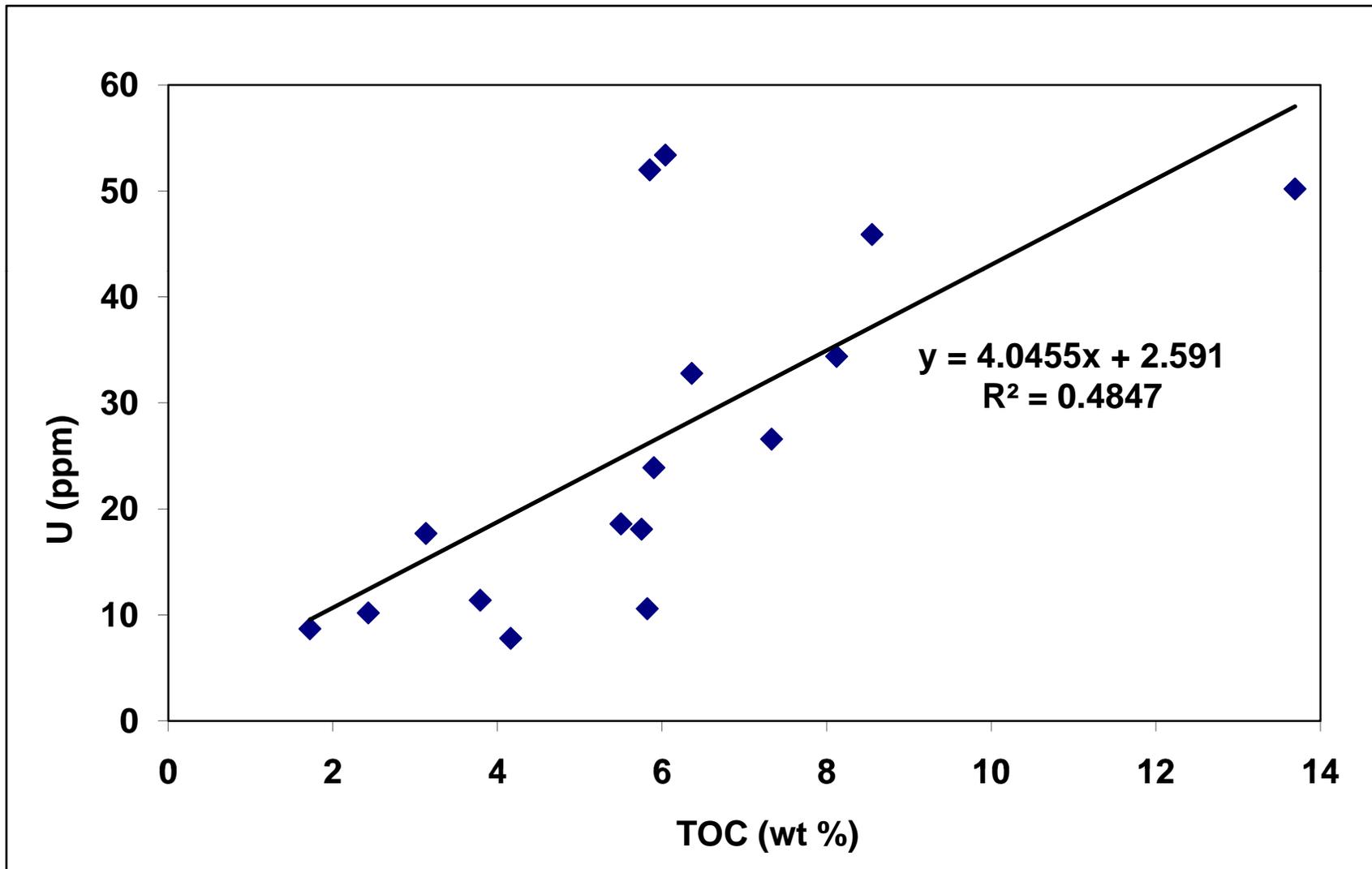
- Mineralogy is dominated by quartz (19-56%), calcite (.3-15%), feldspars (few %), pyrite (.3-7%), and clay minerals (42-69%)
- Clay minerals are dominated by illite, Fe-chlorite, Mg-chlorite, and kaolinite
- Total Organic Carbon (TOC) of samples ranges from 2.4 – 13.7 wt %
- Mineralogy of outcrop and core samples differs slightly
 - Cores contain more calcite (up to 15 wt%)
 - Outcrops contain more quartz (47 wt % vs ~30 wt%)



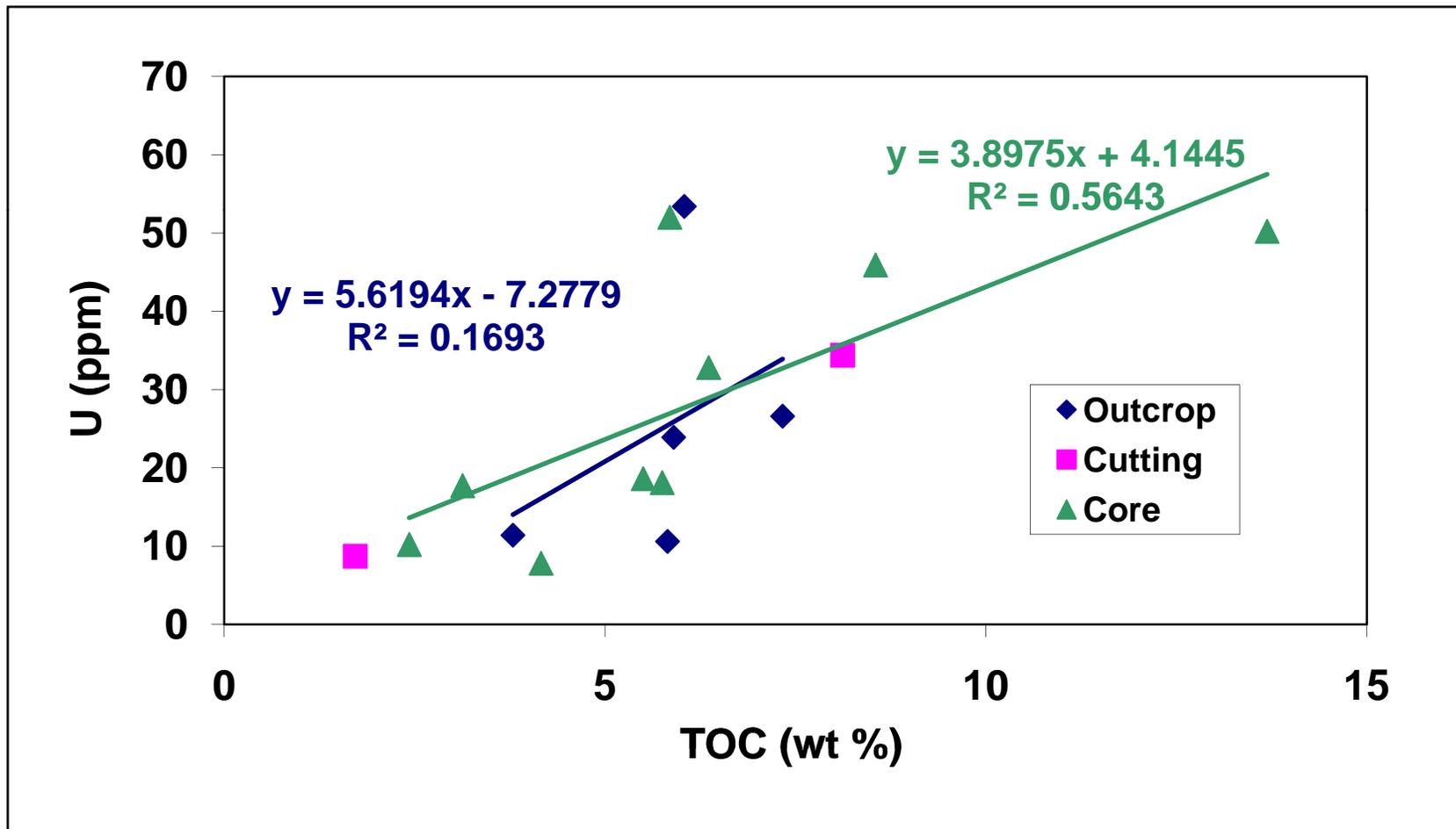
Uranium in the Marcellus Shale

- Uranium concentrations range from 8-53 ppm
- Concentrations up to 100 ppm reported in other studies
- Uranium is elevated due to reducing conditions in the shale which likely favour insoluble U(IV) and/or U sorption onto organic matter
- Uranium is positively correlated to TOC

Uranium vs TOC



Uranium vs TOC

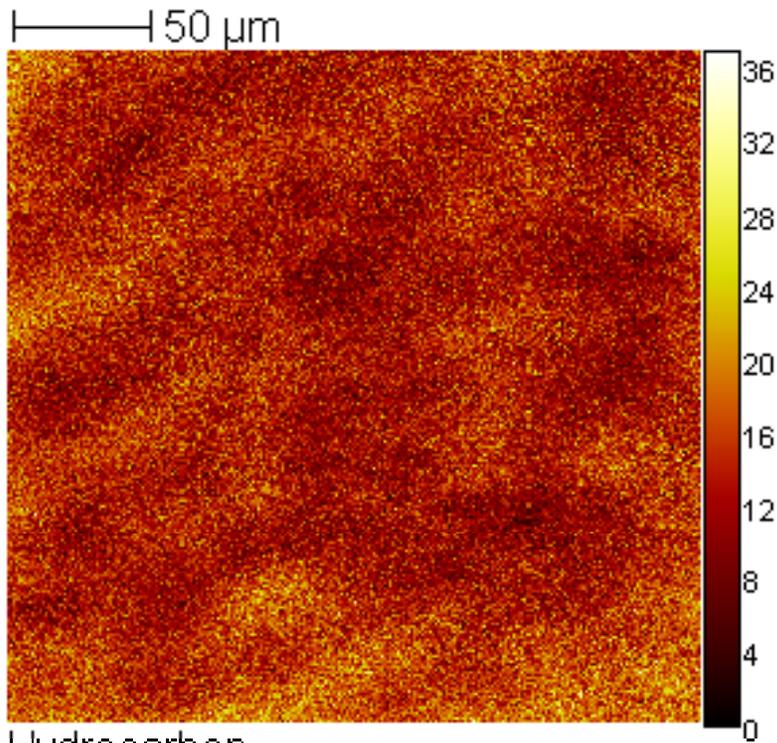


ELEMENT MAPPING TOF SIMS

- Used to identify physical and chemical relationship between metals and organic matter

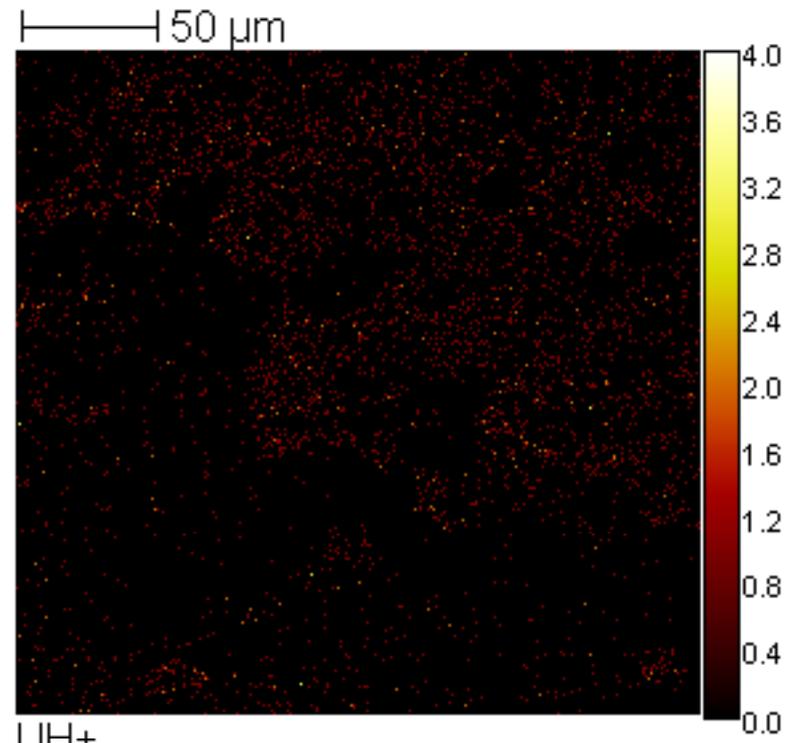


Uranium and Hydrocarbons



Hydrocarbon

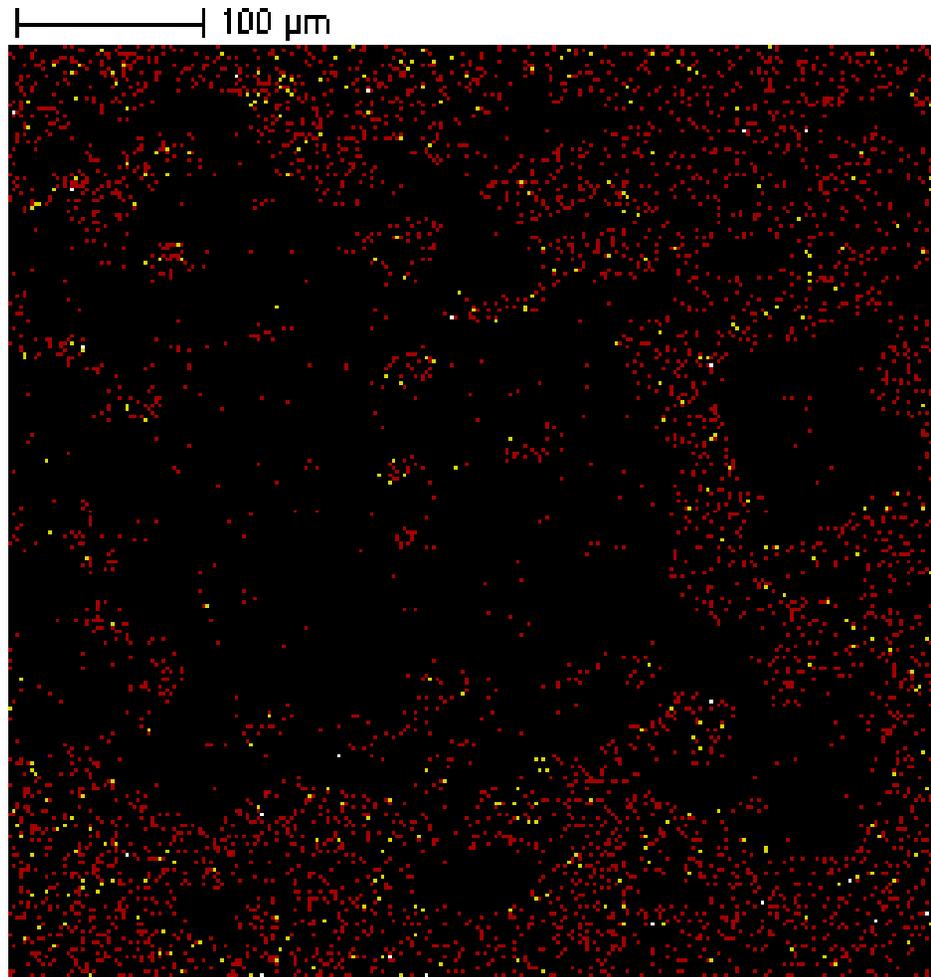
Hydrocarbon



UH+
mc:4 tc:3.80e+3

UH+

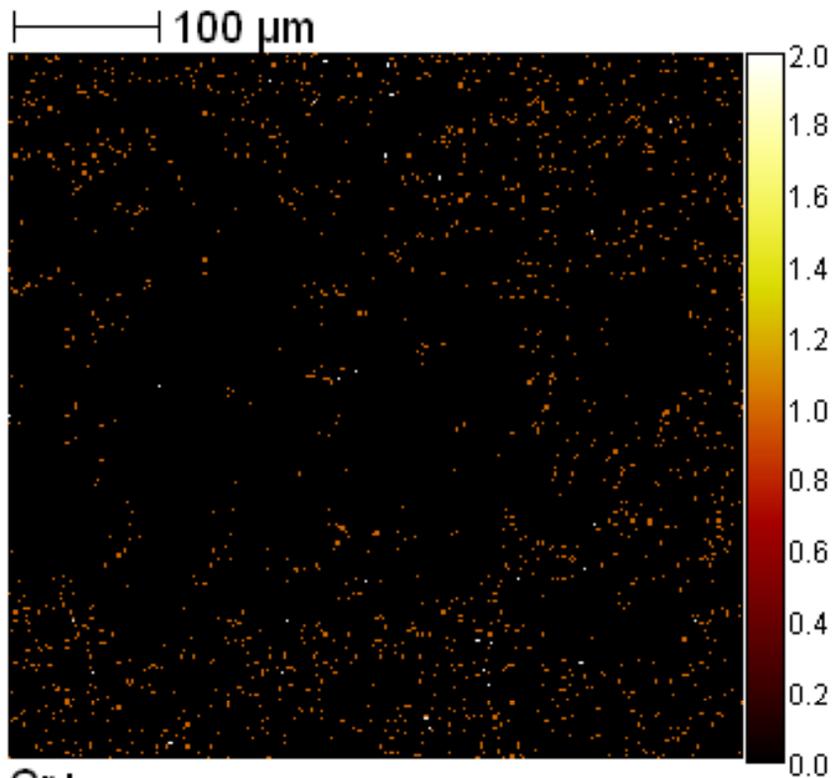
Uranium and Hydrocarbons



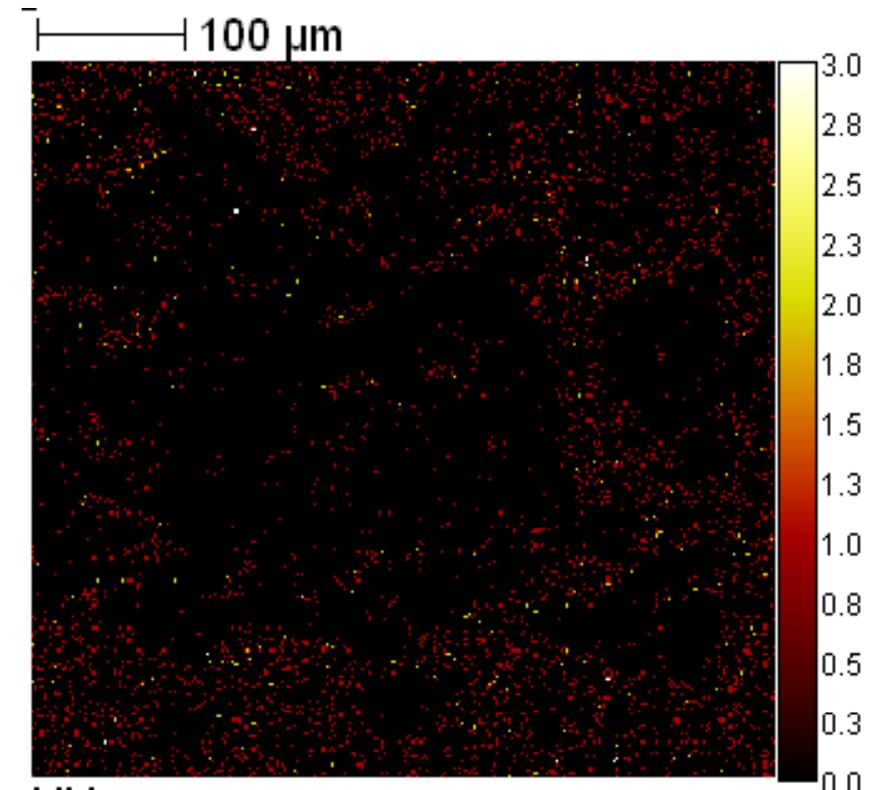
Uranium + Hydrocarbons

mc:3 to:5.10e+3

Chromium and Uranium



Cr+
mc:2 tc:1.53e+3



UH+
mc:3 tc:4.07e+3

Results to Date

- Heavy (and toxic) metals are associated with the organic matter in the Marcellus Shale
- Association is both physical and chemical
- Metal concentrations increase in the most organic-rich shales
- A percentage of the metal is extractable by HCl and oxidizing fluids
- Flowback fluids are going to be “enriched” in these heavy metals

Trace Metal Chemistry and Mobility in the Marcellus Shale

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Drilling and “fracing” of the Marcellus shale causes fluid-rock interactions that have the potential to mobilize metals that are naturally enriched in the shale. While the concentrations of these metals are low, their mobilization from the solid, through redox reactions and leaching, is cause for further study.

In a series of studies, the trace metal geochemistry of the Marcellus Shale and the extractability of select metals through fluid-rock interactions have been determined. The studies were completed on 16 shale samples including outcrop, well core, and well cuttings from western New York and Pennsylvania. Instrumental neutron activation analysis (INAA) was used to determine the concentrations of metals in the shale samples prior to any chemical treatment. The analysis indicates that the Marcellus Shale is enriched in barium, uranium, chromium, and zinc, among other metals (Table 2). For comparison, the maximum contaminant level (MCL) in the United States for barium, uranium, chromium, and zinc are 2 ppm, 30 ppb, 50 ppb, and 5 ppm, respectively. It is likely that the barium concentrations reported here are elevated due to contamination from drilling mud which commonly contains barium. This would explain the very high concentration of barium in cuttings and the increased concentration in core compared to outcrop samples (which would not be contaminated).

Table 2. Selected Metal Concentrations in Marcellus Shale

Metal	Outcrop Average (range) n = 3	Core Average (range) n= 9	Cutting Average (range) n=4	Sample Average (range) n=16
Barium	670 ppm (500-900 ppm)	1000 ppm (*BDL–2000 ppm)	1925 ppm (900-3600 ppm)	1314 ppm (BDL–3600 ppm)
Uranium	30 ppm (11-53 ppm)	28 ppm (10-50 ppm)	17 ppm (9-34 ppm)	26 ppm (9-53 ppm)
Chromium	70 ppm (53 – 100 ppm)	86 ppm (70-100 ppm)	98 ppm (70-120 ppm)	86 ppm (53-120 ppm)
Zinc	515 ppm (*BDL – 660)	526.3 ppm (BDL-2290 ppm)	403 ppm (BDL-530 ppm)	496 ppm (BDL-2290)

*BDL = Below Detection Limit (Ba = 100 ppm, U = 0.5 ppm, Cr = 10 ppm, Zn = 50 ppm)

The concentration of metals in the shale generally increases as the concentration of total organic carbon increases. This is likely because conditions that favor the preservation of organic matter during shale formation also favor the deposition of metals in a reduced state. This is of interest because natural gas developers naturally target regions with the higher concentration of organic matter which are also the most metal-rich.

To determine the extent that these metals could be mobilized during reactions that occur between drilling and/or fracing fluids and the shale, several chemical extractions have been performed. Batch extraction studies were completed using a measured mass of ground and sieved shale and a known volume of chemical extractant. The batch systems were either shaken or stirred for the duration of the extraction (which varied from just a few minutes to 24 hours). Metal concentrations in the shale were measured prior to the extraction test and following the extraction. Also, in some cases metal concentrations in the batch fluid were measured at the end of the extraction study. The extraction studies included: 1) a dilute sodium bicarbonate solution which could remove easily exchangeable ions from the rock, 2) a hydrochloric acid extraction to dissolve carbonate minerals and strongly sorbed metals, 3) a hydrogen peroxide treatment to oxidize organic matter and associated metal, and 4) a sodium dithionite solution which would remove oxide and hydroxide minerals and their associated metals. The results of the sodium bicarbonate study indicated that little to no metal could be solubilized from the shale during a 24 hour reaction. The results of the sodium dithionite study were also negligible because there are so few oxide minerals in the shale. The hydrogen peroxide treatment indicated that some metals were associated with the organic matter in the shale. An average of 20% of the zinc in the samples was solubilized with an extractable range from 3-80%. Additionally, up to 35% of the uranium was solubilized, but a greater amount of uranium could be removed from the outcrop samples compared to the core. Up to 30% of the chromium was removed, but an average of only 8.5% was removed from the shale.

The results of the hydrochloric acid extraction provided the largest amount of data and indicated potential for metals to be solubilized and mobilized from the shale. HCl is used prior to fracing a well to dissolve carbonate cement and increase flow pathways for the natural gas. In this study, finely ground shale was reacted with 3 M and then 1.5 M HCl for a total of two hours. The amount of metal solubilized in the batch solution was measured using inductively coupled plasma mass spectrometry (ICPMS). Additionally, the solid sample was re-analyzed following the extraction test. Interestingly, the results of this study varied depending on whether the sample was outcrop or core; outcrop samples contain up to 70% HCl extractable uranium while core samples contain only about 25% HCl extractable uranium. Zinc and chromium were both moderately extractable in both sample types, up to 60% and 20% respectively. Up to 40% of the barium was removed during the extraction but results vary from sample to sample and are probably affected by contamination from drilling muds.

This study shows that metals may be mobilized from the shale into wastewater produced during natural gas development. Additionally, the results of this study indicate that many of the heavy metals in the shale are potentially leachable and may present a disposal issue. Drill cuttings that are removed during drilling of thousands of feet of well hole need to be properly disposed. These cuttings contain reduced metals that will oxidize over time if exposed to air and water. Proper disposal of these cuttings needs to be considered.