Chemical Associations of Uranium, Chromium and Hydrocarbons in the Marcellus Shale

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Introduction

The Marcellus Shale is a metal and organic-rich shale that was deposited 365 million years ago. It is an important gas reservoir containing 168 trillion cubic feet (TCF) of natural gas of which an estimated 10% is recoverable using directional drilling and hydraulic fracturing (fracing). In this study, I am investigating fluid-rock interactions that occur during well stimulation and production. I hypothesize that fracing fluid can alter the oxidation and speciation of metals in the shale, including uranium and chromium, that may increase their solubility in the subsurface. The lithogeochemistry of 16 core and outcrop samples of the Marcellus Shale collected from western NY and PA has been completed. Batch extraction studies determined that a significant amount of metal in the shale is potentially soluble. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has been used to map the elemental compositions and metal speciation of six of these samples.

Facts

◆ In the last 10 years, the United States produced between 85 and 90 percent of the natural gas it consumed [1].

◆The Marcellus Formation extends 600 miles across the southern tier of New York across Pennsylvania, western Maryland, West Virginia and eastern Ohio.

◆ In the Marcellus formation, natural gas occurs in the pore spaces between individual grains, as well as chemically adsorbed onto the organic matter within the shale.

◆Hydraulic fracturing can inject over 3.5 million gallons of water in to a well.

Background

Previous studies showed that shale is naturally enriched in uranium, averaging 3.2 ppm (mg/kg) (Hallenburg, 1998). However, black shale has a substantially higher uranium content of 4-22 ppm [2]. Historically, black shale has been mined for uranium in Jämtland, Sweden and Sillamäe, Estonia.

Twenty two core, well cutting, and outcrop samples of the Marcellus Shale from NY and PA were analyzed for total organic carbon (TOC) content and trace metal geochemistry. TOC varied between 2.43 wt% and 13.69 wt%. Uranium concentrations ranged from 8.7 ppm to 53.4 ppm. High concentrations of chromium were also present, ranging from 53 ppm to 120 ppm. Up to 70% of the uranium and 30% of the chromium was extractable by dilute HCl. Extractability of the metal is likely a function of the metal speciation in the shale samples.

Methods

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis was used to determine the speciation of uranium and chromium present in three core and three outcrop samples of Marcellus Shale.

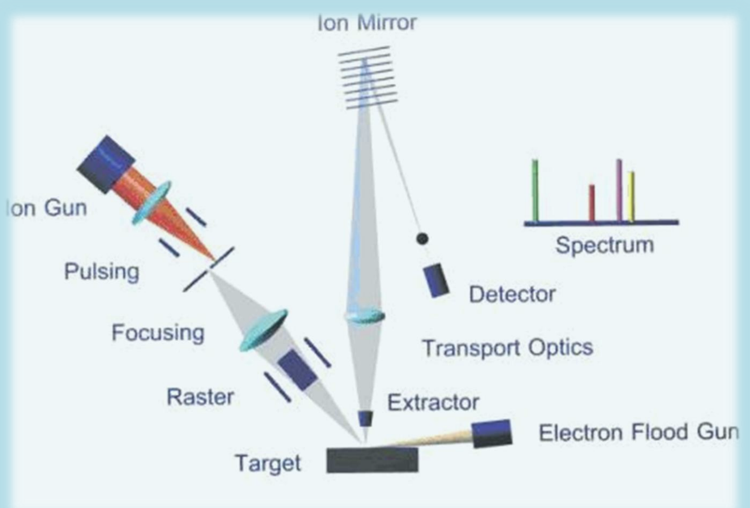

Figure 1: Schematic Diagram of ToF-SMS [3]

ToF-SIMS is a laboratory technique that analyzes the surface composition of solid samples under ultra-high vacuum conditions. ToF-SIMS can be used to distinguish the elemental, isotopic, or molecular composition of samples with minimal sample preparation.

2-D maps of the composition of the samples were created by rastering the ion beam across each sample in X-Y space. Results are both semi-quantitative and qualitative.

Figure 2: ToF-SIMS

Results

ToF-SIMS imagery of core and outcrop samples

Increasing intensity (concentration) is represented by brighter colors on 2-D map

Outcrop Sample S2

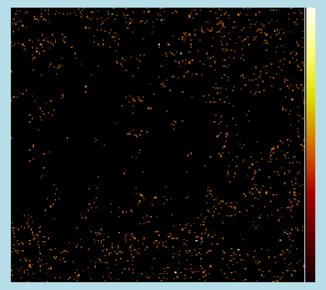

Figure 3A: Cr+

1.53E+3 counts

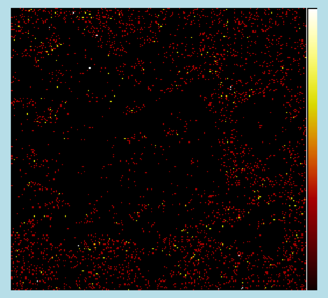

Figure 3B: UH+

4.07E+3 counts

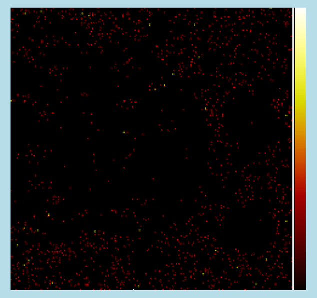

Figure 3C: U+

1.66E+3 counts

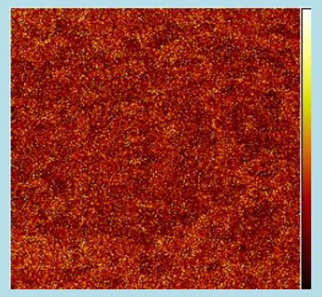

Figure 3D: Hydrocarbons

12E+5 counts

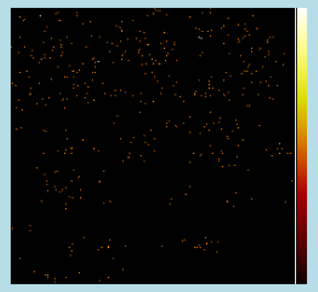

Figure 3E: UO-

4.34E+2 counts

Core Sample A2

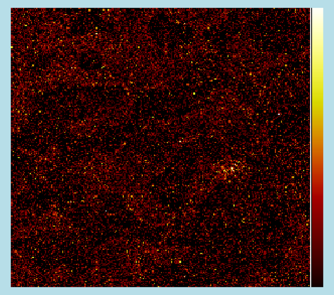

Figure 4A: Cr+

3.77E+4 counts

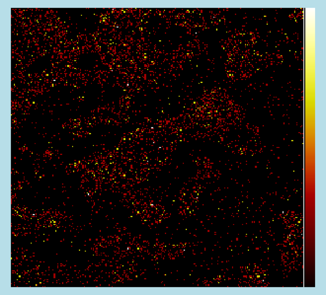

Figure 4B: UH+

6.13E+3 counts

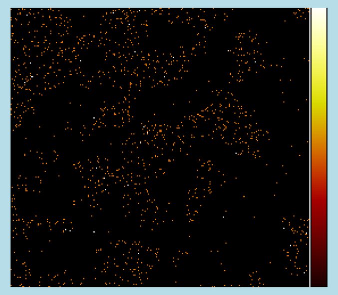

Figure 4C: U+

1.52E+3 counts

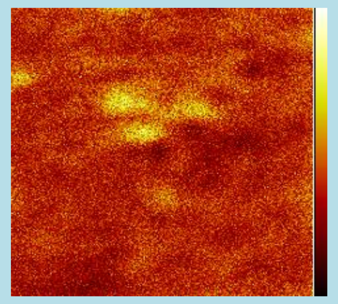

Figure 4D: Hydrocarbons

1.56E+6 counts

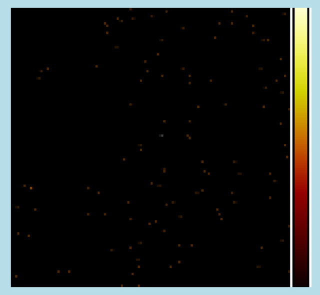

Figure 4E: UO-

1.20E+2 counts

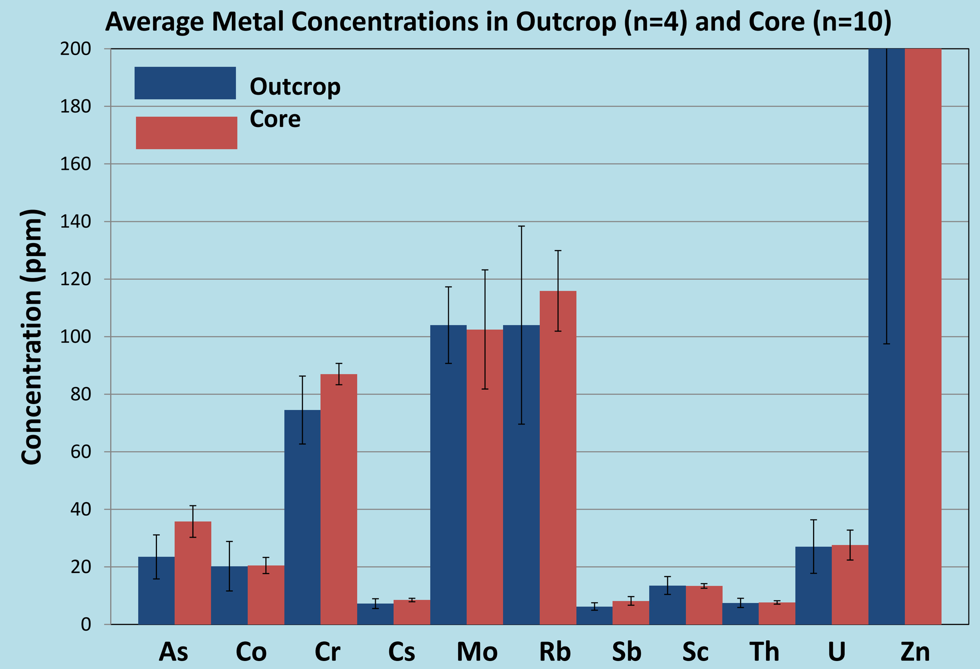

Figure 5: Trace metal concentrations of outcrop and core samples from the Marcellus Shale

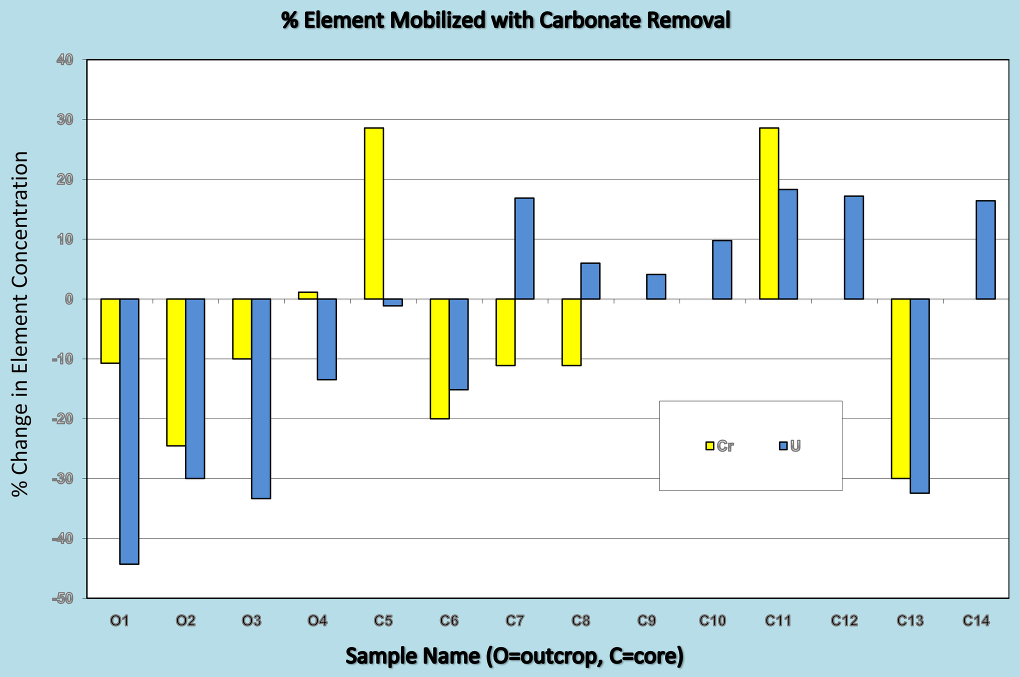

Figure 6: % Cr and U mobilized with carbonate removal in outcrop and core samples from the Marcellus Shale

Conclusion

Six samples were analyzed and 2 sets of results are shown:

In outcrop sample S2, hydrocarbons are shown to be evenly distributed. UH+ had the highest elemental intensity signal with 4.07E+3 count. UH+ was more evenly distributed than UO-, U+ and Cr+.

In core sample A2, hydrocarbons were less evenly distributed. Cr+ had the highest elemental intensity signal with 3.77E+4 counts. Cr+ was much more evenly distributed than UH+, U+ and UO-.

From both samples, we see that UH+ is more evenly distributed that U+ and UO-. It also has a higher elemental intensity signal.

Future Work:

Ten additional Marcellus samples will be collected and lithogeochemistry and TOC of each sample will be analyzed. Chemical maps of uranium, chromium and hydrocarbons will be created by ToF-SIMS 2-D mapping. Afterwards, a synthetic fracing fluid will be created and reacted with the same samples in a rotary shaker for 24 hours. The shale samples will then be rinsed in deionized water, dried at 30ºC for 24 hours, and reanalyzed via ToF-SIMS to determine if fracing fluid changes the speciation of metals in the shale. Additionally, any mobilized metals in batch fluids will be analyzed by ICP-MS.

References

[1] Anonymous, 2005, Liquefied Natural Gas: Understanding the Basic Facts, *in* Energy, U. D. o., Ed.

[2]C. Galindo, L. M., S. Fakhi, A. Nourreddine, A. Lamghari, H. Hannache, 2006, Distribution of naturally occurring radionuclides (U, Th) in Timadhit black shale (Morroco): Journal of Environmental Radioactivity, v. 92, p. 41-54.

[3] Carleton College. www.serc.carlton.edu