Dirty work: Soil formation and isotope fractionation behind Brumbaugh Academic Center

Andrew P. Fornadel(1), Ryan D. Mathur(1), Susan L. Brantley(2)

(1) Juniata College, Department of Geology; (2) The Pennsylvania State University, Department of Geosciences

ABSTRACT:

In order to determine the effects of weathering and the mobility of elements within soils overlying black shales, we conducted a geochemical and physical study of soil developed on the Marcellus Shale. This study provides a basis for understanding the pedogenic processes that have affected the Marcellus Shale. Understanding these processes is essential for the completion of further in-depth geochemical analyses.

Bulk chemistry of the samples was determined by ICP-MS analysis. Using this data, we normalized the elemental proportions to Nb and constructed tau plots to graphically demonstrate the enrichment or depletion of cations compared to the parent material as a function of depth. Geochemical data from this study show that the effect of weathering is greater near the surface of the soil and decreases nearer to the bedrock.

We determined the mineralogy of the soils with X-ray diffractometery (XRD) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) at Juniata College. XRD patterns show that the dominant mineralogy in the samples consists of quartz, illite, montmorillonite, muscovite, and biotite. Mineralogical variety increases in samples closer to the bedrock, which include phases of todorokite and trona. SEM with EDS analysis of a sample from ~104cm depth complemented the mineralogy reported by XRD and revealed the presence of salts containing iron, chlorine, and sulfur. These minerals present a possible source for metals found in the soil profile.

SEM images were taken of powder mounts of selected samples to assess the physical effects of weathering in relation to depth in the soil cores. Images of samples closer to the surface show angular and irregular grain shape, a result of active weathering and water percolation. Images of samples close to the bedrock interface show equant and euhedral grains due to the absence of physical weathering.

We developed a protocol for the extraction of Cu from the dissolved silicate matrix of the soil using ion exchange resins. All reported δ^{65}Cu yielded >90% of the Cu from the original soil. δ^{65}Cu values range from -0.49‰ to 1.00‰. The enrichment of Cu in the upper soils coupled with high δ^{65}Cu values suggests that Cu was biologically sequestered.

INTRODUCTION:

The Marcellus Shale is a Middle Devonian, carbonaceous black shale through its geographic extent (Faill, 1998). It was deposited during a period of rapid transgression in anoxic waters less than 300 ft. deep (Potter et. al., 1981). The anoxic conditions provide for the black, organic-rich nature of the shale.

Because existing geochemical data related to the Marcellus Shale and its associated soils is scant, we devised an exploratory geochemical survey. The purpose of our study is to develop a baseline for understanding how weathering processes have effected the Marcellus Shale during the development of its overlying soils. Chemical and mineralogical data show the vertical transport of elements in the soil and changes in mineralogy with depth. Electron micrograph images of the soils help to define the extent to which weathering occurs through the soil profile.

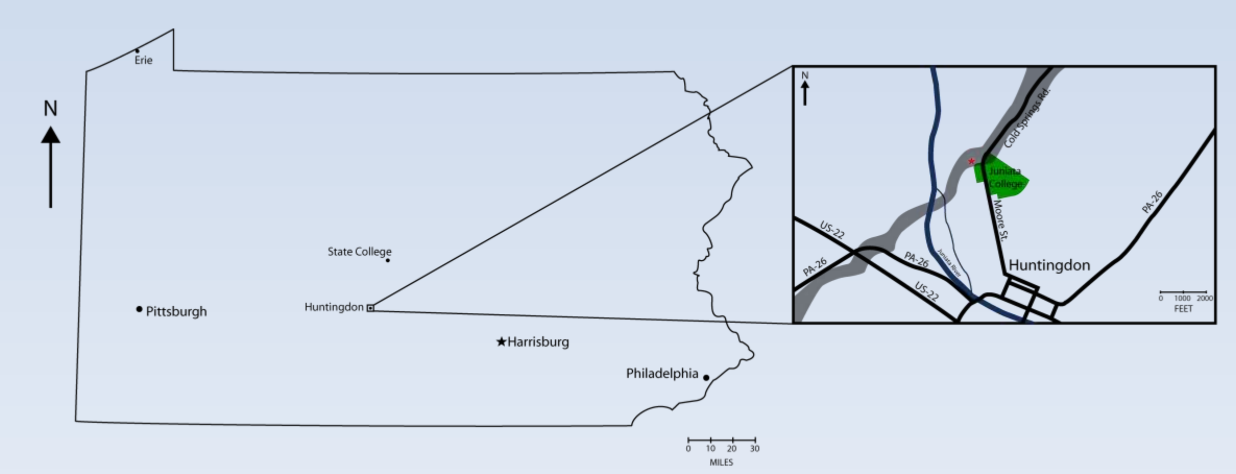


Figure 1: Map of Pennsylvania and Huntingdon. The geographical extent of the Marcellus Shale is highlighted in gray. Our research area is denoted by the red star.

METHODS:

Our sampling site is on the campus of Juniata College. We used a hand auger to drill a core through 194cm of soil to the interface with the bedrock and sampled soils at various depths along the core. Through the core, we collected 16 soil samples and 1 sample of parent material.

To calculate bulk density of the top three soils, the mass of a known volume of soil was measured. The samples were dried in an oven at 105 C for 24 hours, their dry mass measured, and density calculated.

For all other analyses we air-dried the soils for 72 hours. We then crushed, homogenized, and sieved the soils to a ≤ 75µm fraction. The soils were prepared for individual analyses based on the following protocol:

Bulk Chemistry:
•1g of the ≤ 75µm fractions of each soil were analyzed for bulk chemistry by ICP-MS.
•Chemical analyses were normalized to Nb and plotted as tau plots to determine enrichment and depletion of elements through the soil profile in relation to their proportion in the parent material (Anderson et. al., 2002).
•Tau values were calculated by:

$$\tau = \left[\frac{\text{Conc. Element Sample } x \text{ Conc. Nb Parent}}{\text{Conc. Element Parent } x \text{ Conc. Nb Sample}} \right] - 1$$

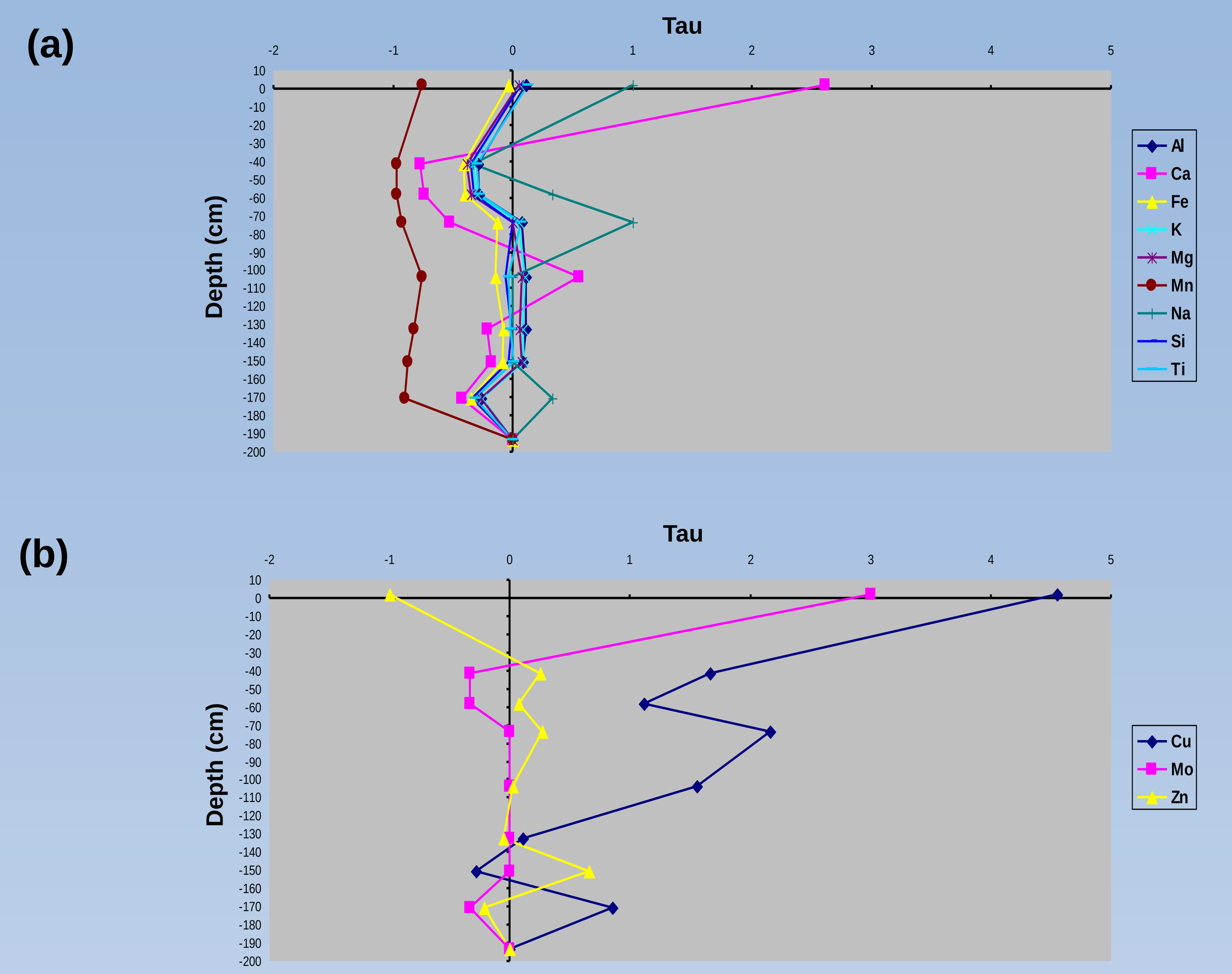
XRD:
•We mounted a portion of the 75µm fraction of each soil as a packed powder mount to avoid preferential orientation of the clay minerals (Moore and Reynolds, 1997).
•We performed XRD analysis from 2° to 80° 2Θ using a step of 0.02° at a rate of 2.50° per minute.

SEM with EDS:
•We made epoxy mounts of eight samples and polished them successively with 600 and 1000 grits, followed by 6, 3, and 1 µm grits. An epoxy mount of a sample from 104cm depth was carbon coated and analyzed on the SEM with EDS.

Isotopic Measurements:
•A portion of the ≤ 75µm fractions of soils were dissolved in HF followed by aqua regia and dried.
•Dried samples were dissolved in a solution of HCl and H_2O_2.
•Cu was extracted from solution with >90% yield using ion exchange resin.
•δ^{65}Cu‰ were measured in triplicate on a multicollector mass spectrometer at Washington State University.
•The isotope values were averaged and plotted versus depth.
•Mass balance was calculated by:

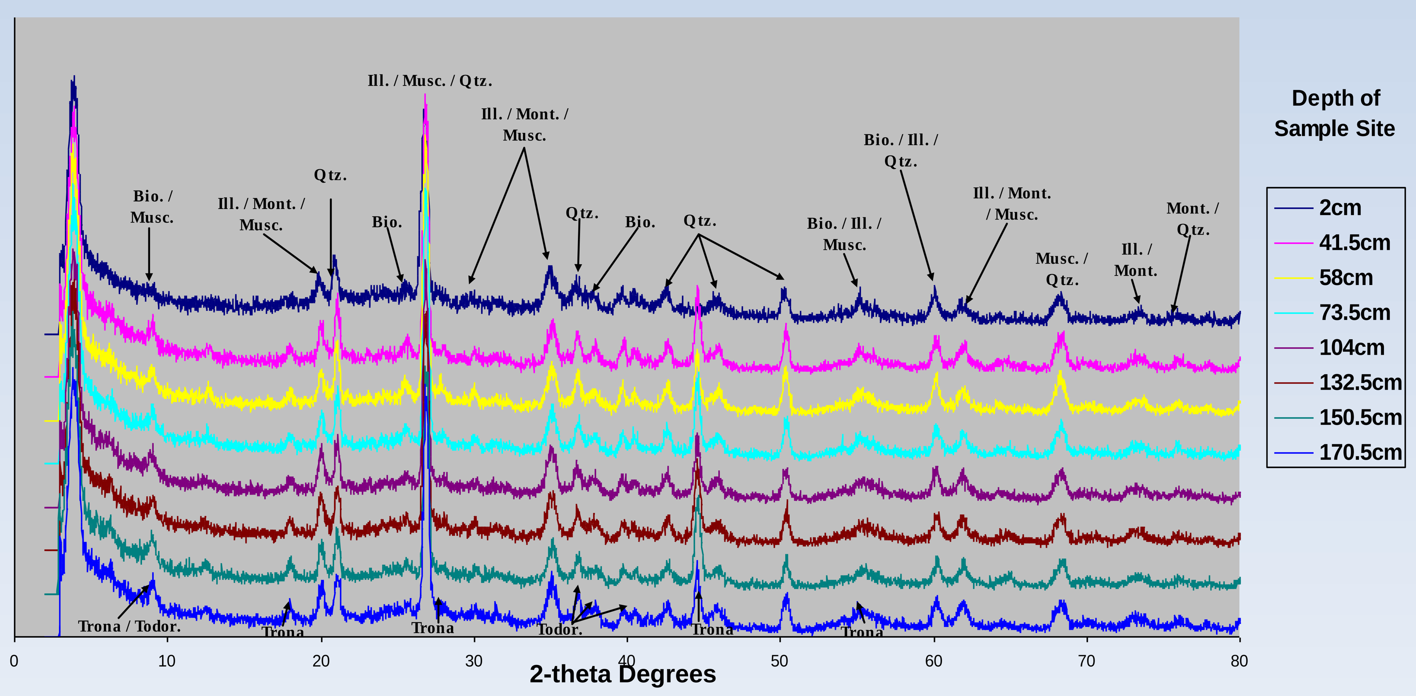
$$\sum_{\text{Over Total Depth}} \left(\frac{\text{Conc.Cu Sample}}{\sum \text{Conc.Cu Total}} \right) x\, \delta^{65}\text{Cu Sample} = \delta^{65}\text{Cu Parent}$$

Bulk Chemistry Results:



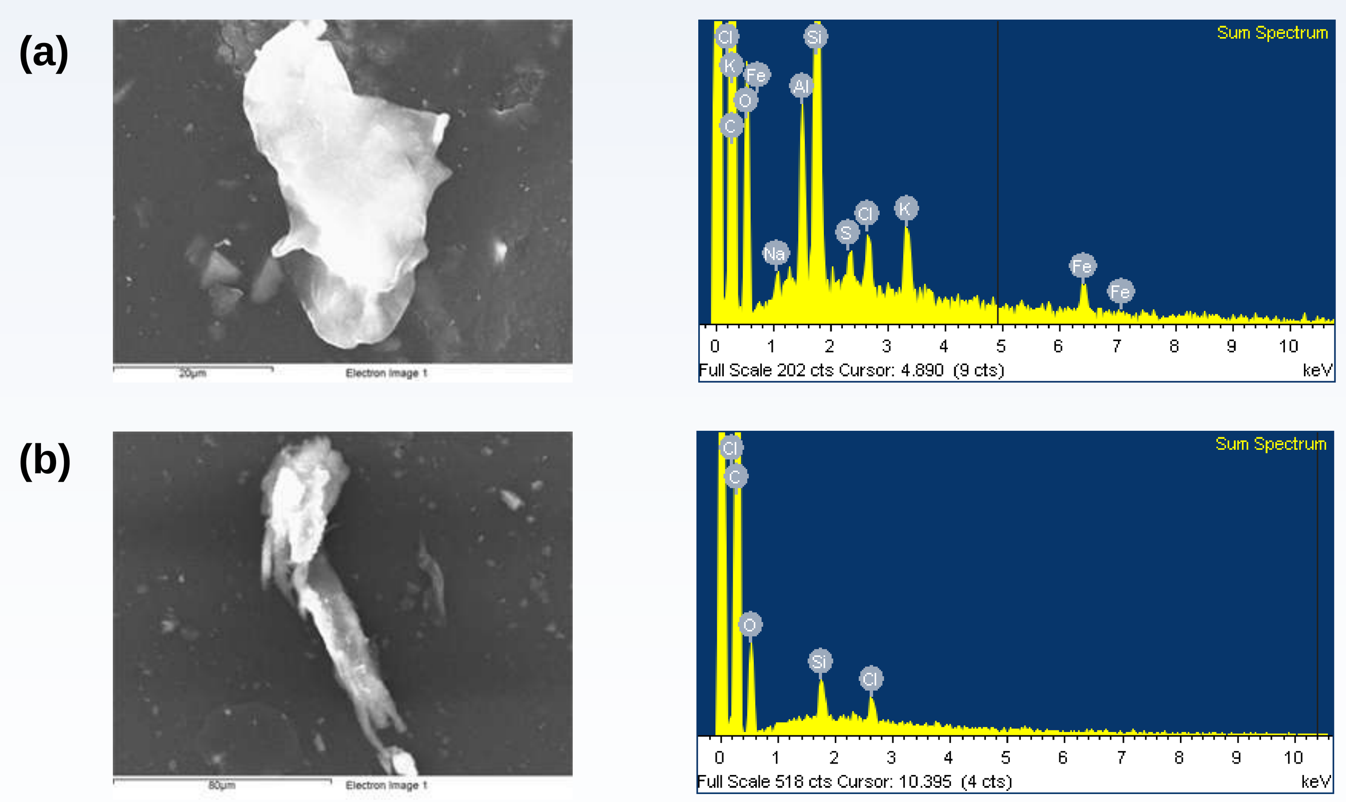
Tau plots showing enrichment and depletion of major oxides (a) and selected metals (b) with depth in the soil profile.

XRD Results:



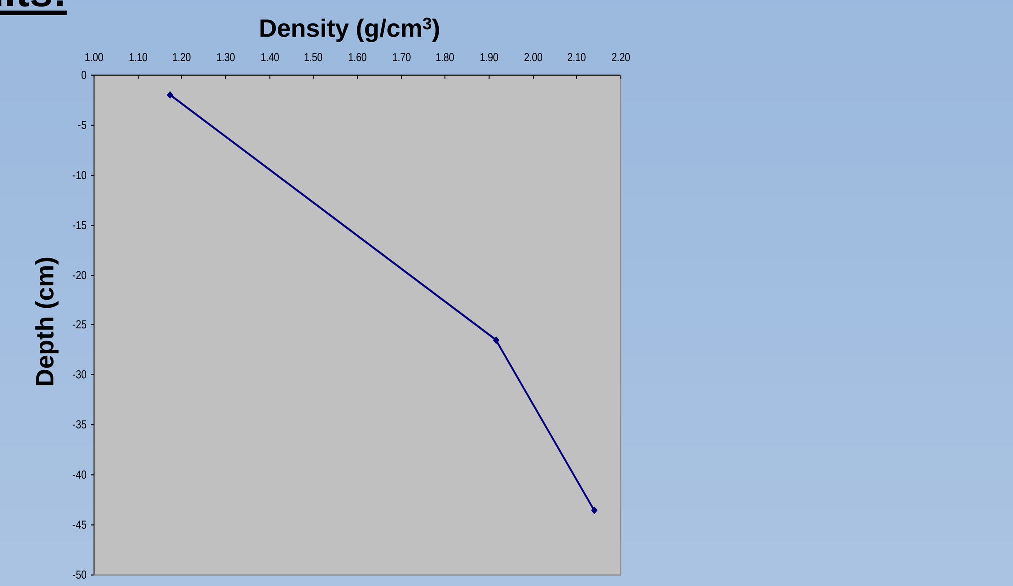
XRD patterns for samples taken from various depths and demonstrates changes in mineralogy. Minerals common to all samples are labeled at the top. Minerals that become present with depth are labeled at the bottom. Peaks on the images are labeled with mineralogy. Qtz. – Quartz; Mont. – Montmorillonite; Ill. – Illite; Todor – Todorokite; Bio. – Biotite; Musc. – Muscovite.

SEM with EDS Results:



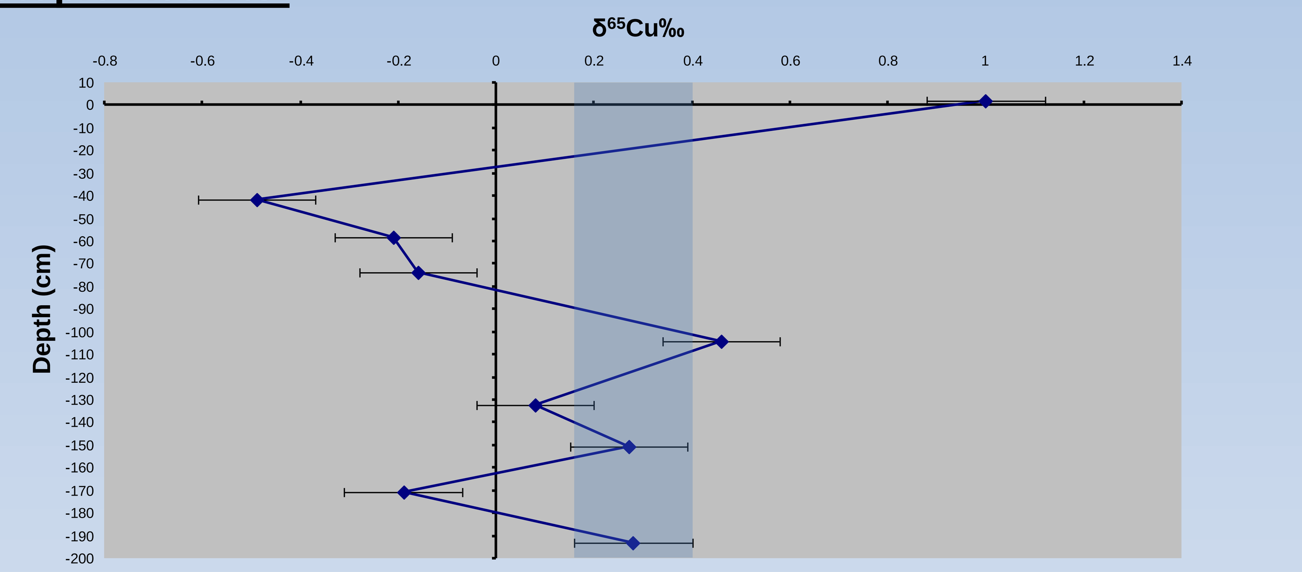
Electron micrographs and associated EDS spectra for selected grains from a sample from a depth of 104cm. The spectra of grain (a) notably shows the presence of Cl, Fe, and S; the spectra of grain (b) notably shows the presence of Cl.

Bulk Density Results:



Soil density as a function of depth for the upper-most three samples. Density data could not be collected for the remaining samples.

Isotopic Results:



δ^{65}Cu measurements with depth in the soil profile. The isotopic signature of the parent material is shown in the blue box.

DISCUSSION:

Bulk Chemistry:
•Tau values for most oxides reflect depletion profiles indicating mineral dissolution near the surface of the soil. (Brantley, et al., 2007)
•Ca and Na are extremely enriched near the surface, but like the other oxides, trend towards depletion with depth in the soil.
•The tau profile pattern of Cu is mimicked by Mo, but not Zn.
•This indicates that biological processes responsible for the uptake of Cu similarly fix Mo.

XRD:
•XRD patterns show that the number and variety of mineral species increases with depth.
•Biotite, Quartz, Montmorillonite, Muscovite, and Illite common in all soils.
•Todorokite, and Trona are present in lower soils.

SEM with EDS:
•Spectra show the presence of grains containing S, Fe, and Cl.
•These minerals could provide sources for metals found in the soils.

Bulk Density:
•As expected, the trend in bulk density shows that upper soils become more dense with depth.

Isotopic Data:
•In general, δ^{65}Cu was high in the upper-most organic rich soil, bolstering the evidence for biological sequestration. (Mathur et al., 2005)
•Mass balance of the copper concentrations and isotopic values suggest that all of the copper within the soil profile originated from the bedrock and is being sequestered biologically near the surface.

REFERENCES:

Anderson, S. P., Dietrich W. E., and Brimhall G. H. J. (2002) Weathering profiles, mass-balance analysis, and rates of solute loss: Linkages between weathering and erosion in a small, steep catchment. Geol. Soc. American Bull. 114, pp. 1143-1158.

Brantley, S. L., Goldhaber, M. B., and Ragnarsdottir, K. V. (2007) Crossing Disciplines and Scales to Understand the Critical Zone Elements, 3 (5): pp. 307 - 314.

Faill, R.T. (1998) The Geology of Pennsylvania: Harrisburg, Pennsylvania Geological Survey, 888p.

Mathur, R., Ruiz, J., Titley, S., Liermann, L., Buss, H., and Brantley, S.(2005) Cu isotope fractionation in the supergene environment with and without bacteria. Geochimica et Cosmochimica Acta, 69 (22): pp. 5233 – 5246.

Moore, Duane M., Reynolds Jr., Robert C. (1997) X-Ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd Ed.: New York, Oxford, 378 p.

Potter, P. E., Maynard, J. B., and Pryor, W. A. (1981) Sedimentology of gas-bearing Devonian shales of the Appalachian Basin: Morgantown, WV, U.S. Department of Energy, USDOE/METC-114, 43 p.

ACKNOWLEDGEMENTS:

This study was based upon work supported by Juniata College, the Center for Environmental Kinetics Analysis, and the National Science Foundation under Grant No. CHE-0431328.

Juniata College, 1700 Moore Street, Huntingdon, Pennsylvania 16652
The Center for Environmental Kinetics Analysis, The Pennsylvania State University, 2217 EES Building, University Park, Pennsylvania 16802