

Re-Os Molybdenite Ages for the Antietam Reservoir, Eastern Pennsylvania, a Story of Open System Behavior Re-Os Isotopes in Molybdenite

By Gregory Pierotti, Ryan Mathur, Robert C. Smith II, and Fernando Barra
 Dept. of Geology, Juniata College, Huntingdon PA 16652
 Contact: pierogm1@juniata.edu or mathur@juniata.edu

Abstract:

The Reading Prong is an upland physiographic province located in New York, New Jersey, and Pennsylvania. Lithologically it includes a wide variety of intrusive igneous and metasedimentary gneisses that were metamorphosed during the circa 1.1 Ga Grenvillian orogeny and well as a resistant, overlying Cambrian arkose and quartzite known as the Hardyston Formation. In order to further understand the geochronology of the area, Re-Os molybdenite ages were obtained from dikes crosscutting presumed Byram Intrusive Suite near the Antietam Reservoir, Berks County, Pennsylvania. The Re-Os data can be separate into two groups: 1) Samples with low concentrations of Re and Os (0.25-1 ppm and 0.003-128 ppm respectively) that yielded non-viable geologic ages. 2) Samples with higher concentrations of Re and Os (12 ppm and 0.426 ppm respectively) that yielded a 'reasonable' age of 975 ± 2.4 Ma. SEM with EDS analyses from the first group revealed predominantly molybdenite, with intergrown micron sized blebs of powellite, ferrimolybdenite, and Mg silicates. None of these latter minerals were found in the second group of samples that yielded reasonable ages. This study further confirms the notion that molybdenite samples can be isotopically altered and this disequilibrium can be identified by the presence of supergene molybdenum minerals such as powellite and ferrimolybdenite. The 'reasonable' Re-Os age is younger than the reported age of the Byram Intrusive Suite but is approximately coeval with the youngest of several xenocryst zircon tip U/Pb concordant dates (J. Ramezani, personal communication to R.C. Smith, II), also in a crosscutting dike, from Lehigh County, Pennsylvania, containing minor chevkinite and trace molybdenite ($2H1:3R = 10:1$, Smith, 1978). The ~975 Ma ages likely represent post-Grenvillian extension.

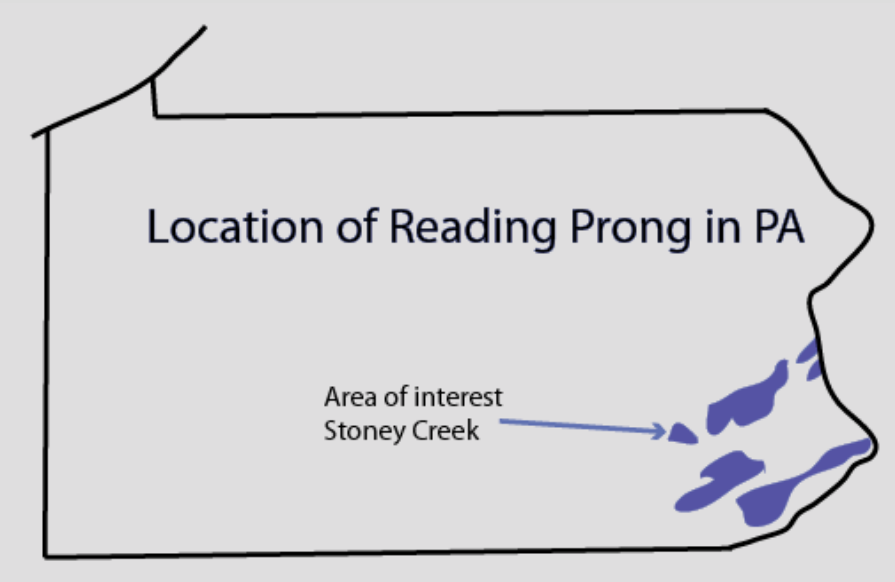


Figure 1:

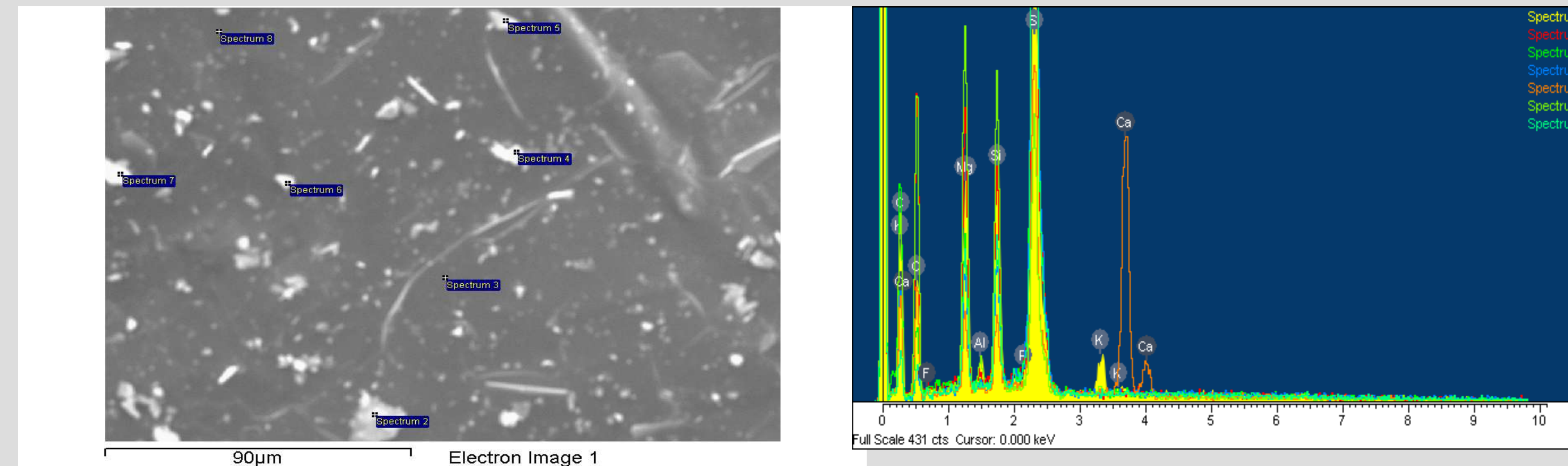
Introduction:

The purpose of this research was to determine the ages and formation of the disseminated molybdenite in rocks located in southeastern Pennsylvania. Specifically, the area of this study is located in a physiographic upland known as The Reading Prong, the western, Berks County portion of which is a relatively unstudied (figure 1). The Reading Prong portion of the Pennsylvania state geologic map (Berg et al., 1980) is based mainly on mapping done by T. V. Buckwalter in the 1960's. The eastern portion of the Reading Prong in Pennsylvania has been mapped in more detail by Avery A. Drake, U.S.G.S., and much of the New Jersey portion by him in collaboration with Rich A. Volkert of the New Jersey Geological Survey. Smith and Barnes (1989) described only the uranium- and thorium-enriched portions of the Reading Prong in Pennsylvania, but did provide mineralogical and elemental data for a number of molybdenite occurrences. They described one pyritic leucogneiss slightly enriched slightly in U, Th, and Mo from just to the south of the sampling done for the present study as sample RP-2, a composite chip sample collected from a 4.85-m long interval. They provide elemental and mineralogical data for the 3.7 kg composite. Smith (2003) described next youngest extensional volcanics in the Reading Prong of Pennsylvania as the 602.3 +/- 2 Ma Rittenhouse Gap Felsite and Tunnel Mine Metadiabase. These he interpreted as bimodal extensional volcanics related to northeastward migration of the hotspot responsible for the Mount Rogers and Robertson River volcanic areas. At Rittenhouse Gap, Berks County, there is a minor, apparent late stage of molybdenite and fluorite mineralization that overprints the mined iron oxides. By determining Re-Os isotope data, obtaining SEM elemental mapping and field data, we determined the age of the Antietam Reservoir molybdenite. Supergene elemental and isotopic alterations were also be determined using these techniques.

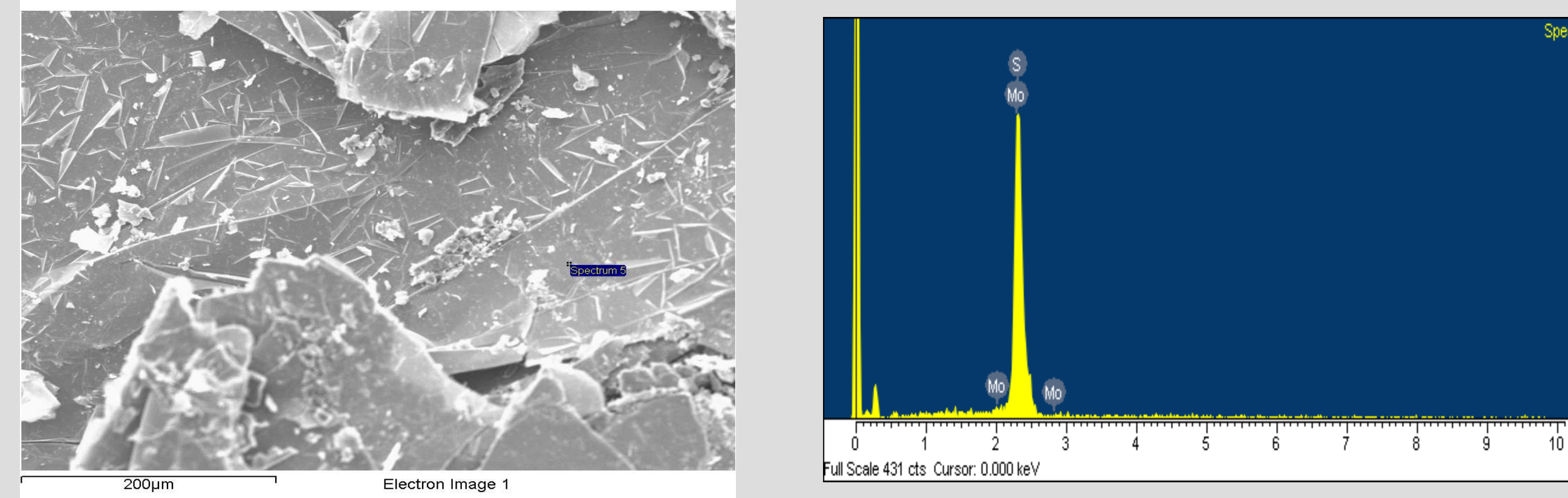
Most of the molybdenite studied were collected from the area of Antietam Reservoir, Stony Creek Mills, northeast of Reading, Pennsylvania. Montgomery (1969) summarized molybdenite occurrences in the Reading Prong and elsewhere in southeastern Pennsylvania. The Antietam Reservoir molybdenite occurrence was first described by Smith (1975). He reported 0.15% Mo and 0.05% Cu in a representative, 5 kg composite of 2.5 cm chips collected prior to countless visits by enthusiastic mineral collectors. The host rock at Antietam Reservoir is presumed to be a late stage of the Byram Intrusive Suite, but the area has not been mapped using modern methods. At Antietam Reservoir, the Byram is a coarse-grained hornblende-plagioclase-quartz granitic gneiss. Traditionally correlated with the well known Grenvillian-age rocks of Canada, the Reading Prong covers an area that includes much of the northern New Jersey and even areas north into New York State. Geologically complex, the ages determined provide geochronological evidence for minor, slightly post-Grenvillian igneous activity in the area.



Figure 2:



Image(A,B,C) Bad Results



Image(D) Good Results

Sampling and methods:

Molybdenite from four hand specimens (labeled Ant.1-4) was analyzed. Molybdenite occurs in hexagonal blebs (Image 1) within plagioclase rich dike that cross cuts the gneiss. Approximately 0.05g of sample were hand picked, separated, and dissolved in carius tubes (Shirey and Walker, 1995) for Re-Os analysis. The Os was extracted by a two stage distillation process and Re through two different ion exchange chromatographic columns (process described in Mathur, 2000). Concentrations of Re and Os were determined by isotope dilution and measured on a negative thermal ionization mass spectrometer at the University of Arizona. The ages of mineralization were determined by assuming no initial ^{187}Os and a decay constant for Re of $1.66 \times 10^{-11} \text{ yr}^{-1}$ (Smoliar et al., 1996).

To characterize the minerals, we separated individual hexagonal flakes of molybdenite (Image 2) for X-ray diffraction (XRD) and scanning electron microscopy (SEM) with EDS. Samples were powdered for XRD analysis and run on a Scintag V X-ray diffractometer at Juniata College. Flakes of molybdenites were attached to carbon tape and coated with carbon for SEM analysis.

Sample	Total Re (ppm)	^{187}Re (ppm)	^{187}Os (ppb)	Age (Ma)
#1	0.438	0.257	44.41	9570
#2	0.661	0.416	3.91	5615
#3	1.500	1.0001	461.16	2276
#4	12.632	7.942	128.686	975 +/- 5

Table 1: Re-Os Concentrations and their correlating ages

Results:

Four samples of molybdenite were analyzed, concentrations of Re and Os varied from 0.257-7.9 ppm and 0.03-0.461 ppm respectively (Table 1). Three of the samples yielded geologically unreasonable ages (samples 1-3) and sample 4 yielded an age younger than the surrounding metamorphic rocks (Figure 2). XRD analyses of the samples revealed that the molybdenite samples are 2H crystal structure. EDS analyses of these samples reveal differences between the samples that yielded geologically unreasonable ages (ages older than the age of the earth; sample 1-3) and the age that fits within the geochronology of the area (975 ± 5 MA; sample 4). Samples 1-3 contain over/intergrowth of Mg-Fe silicate minerals (Image a,b), powellite, Fe-oxides, and ferrimolybdenite on the borders of the grains. In comparison sample 4 (Image c) does not contain intergrown silicates, and hexagonal crystal habits can be seen in the image.

Discussion:

McCandless et al. 1993 first suggested that supergene processes can lead to the loss of Re in molybdenite. The molybdenite samples 1-3 that contain ferrimolybdenite and other silicate minerals have significantly less Re along with yielding unreasonable geologic ages. We interpret these results as an indication that the Re-Os isotope system was opened by the intense weathering (as evidenced by the powellite and ferrimolybdenite), these mineral grains experienced. In contrast to these three samples, sample 4 did not contain mineralogical evidence of intense weathering. The sample contained significantly more Re (nearly twice as much) and yielded a reasonable geologic age. We interpret that the Re-Os system in this sample did not open. The age is slightly younger than the ages found for the host rocks in the Reading Prong (Figure 2). The age could be indicating some late thermal pulse associated

with extension affecting the region of the orogenic event associated with the Grenville.

References:

- Berg, T. M. and others, 1980, Geologic map of Pennsylvania, 1:250,000, Pennsylvania Geological Survey, 4th series.
- Mathur, R., 2000, Re-Os isotopes of base metal porphyry deposits. University of Arizona, thesis, 153p.
- McCandless, T.E., Ruiz, J., and Campbell, A.R., 1993. Rhenium behavior in molybdenite in hypogene and near-surface environments: implications for Re-Os geochronology. *Geochimica et Cosmochimica Acta*, 57: 889-905.
- Montgomery, Arthur, 1969, Molybdenite in The Mineralogy of Pennsylvania 1922-1965, The Mineralogical Society of Pennsylvania, p. 75-79.
- Shirey, S., and Walker, R., 1995, Carius Tube digestion for low blank rhenium-osmium analysis: *Analytical Chemistry*, v. 67, p. 2136-2141.
- Smith, II, R. C., 2003, Late Neoproterozoic felsite (602.3 Ma) and associated metadiabase dikes in the Reading Prong, Pennsylvania, and the rifting of Laurentia, *Northeastern Geology and Environmental Sciences*, v. 25, no. 3, p. 175-185.
- Smith, II, R. C., 1978, Chevkinite in The Mineralogy of Pennsylvania 1966-1975, Friends of Mineralogy, Region III, p. 69-76.
- Smith, II, R. C., 1975, New molybdenite occurrence in Berks county, Pennsylvania, *Pennsylvania Geology*, v. 6, no. 6, p. 16.
- Smith, II, R. C. and Barnes, J. H., 1989, Geology and mineralogy of uranium and thorium occurrences in the Reading Prong of Berks, Lehigh, and Northampton counties, Pennsylvania, *Pennsylvania Geological Survey*, 4th ser. Unpublished Mineral Resources report.
- Smoliar, M., Walker, R., and Morgan, J., 1996, Re-Os ages of group IIA, IIIA, IVA, and IVB Iron meteorites. *Science*, v. 271, p. 1099-1102.