Re-Os Evidence Used to Link Regional Mineralization Process to the Chesapeake Bag Bolig’s Impact in the Northeastern United States

The Pennsylvania State University
University of Maryland
University of Virginia
Virginia Polytechnic Institute & State University
West Virginia University

The Pennsylvania State University
The Thomas D. Larson Pennsylvania Transportation Institute
Transportation Research Building ❖ University Park, PA 16802-4710
Phone: 814-865-1891 ❖ Fax: 814-863-3707

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7. Author(s) Ryan Mathur, David P. Gold, Chad J. Ellsworth, Arnold G. Doden, Marc Wilson, Joaquin Ruiz, Barry Scheetz

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16. Abstract

Re-Os isotope measurements of sulfide minerals from 10 occurrences that span a radial distance of over 200 Km serve to geochemically link epithermal mineralization in Pennsylvania to an Eocene event. The most likely geologic event that could have influenced the area during the Eocene is the Chesapeake Bay impact event. The significance of the discovery is twofold: to date no epithermal mineralization has been linked to the Chesapeake Bay impact nor has the process been clearly identified throughout the region. The results effect road construction plans for PA, MD, and VA near the meteor impact site because mineralization could occur in any age strata that lie along fracture traces identified in this contribution.

17. Key Words

Meteor impact, ore deposits, Re-Os, sulfides

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Re-Os evidence used to link regional mineralization processes to the Chesapeake Bay Bolig's Impact in the Northeastern United States

Ryan Mathur[1] David P. Gold[2] Chad J. Ellsworth[2] Arnold G. Doden[3] Marc Wilson[4] Joaquin Ruiz[5] and Barry E. Scheetz[2]

[1] **Ryan Mathur**, Department of Geology, Juniata College, Huntington, PA

[2] **David P. Gold**, Department of Geosciences, The Pennsylvania State University, University Park, PA

[2] **Chad J. Ellsworth**, Department of Civil Engineering, The Pennsylvania State University, University Park, PA

[3] **Arnold G. Doden**, Geologic Mapping and Resource Evaluation, Inc., State College, PA

[4] **Marc Wilson**, Carnegie Museum of Natural History, Hillman Hall of Minerals, Pittsburgh, PA

[5] **Joaquin Ruiz**, Department of Geosciences, University of Arizona, Tucson, AZ

[2] **Barry E. Scheetz**, Department of Civil Engineering, The Pennsylvania State University, University Park, PA

Abstract:

Re-Os isotope measurements of sulfide minerals from 10 occurrences that span a radial distance of over 200 Km serve to geochemically link epithermal mineralization in Pennsylvania to an Eocene event. The most likely geologic event that could have influenced the area during the Eocene is the Chesapeake Bay impact event. The significance of the discovery is twofold: to date no epithermal mineralization has been linked to the Chesapeake Bay impact nor has the process been clearly identified throughout the region.

Keywords: Meteor impact, ore deposits, Re-Os, sulfides

Introduction:

During the construction of a major interstate road (I-99) in Centre County, Pennsylvania (Fig. 1) an epithermal pyrite deposit was unearthered. The study by (Mathur, 2008) examined the origin of the sulfide mineralization at this location. With Re-Os data measured in sulfide minerals and fluid inclusion data from cogenetic quartz, they interpreted a younger 33.8 ± 4MA, high temperature (>200°C) mineralization event (represented by fault breccia pyrite) overprinted the Mississippi Valley type mineralization (termed MVT and represented by vein pyrite). The timing of the younger mineralization event coincides with two Cenozoic events in the Appalachian Basin: the Chesapeake Bay impact and Eocene volcanism in the southern portion of the Nittany anticlinorium (Dennison JM, 1971).

The significance of the overprinted Eocene age becomes apparent by examination of previous models that described sulfide deposit genesis related to older mineralization events. Two timeframes for mineralization have been suggested for MVT deposits in the Appalchians: 1) Radiometric dates from alteration silicates indicate that mineralization occurred in the late Permian associated with the Alleghanian Orogeny (Hearn PP, 1987), and 2) Structural geology (Kesler SE, 1990) indicate a Devonian age.

Traditional models of sulfide deposition in the area have favored two different models (similar to the genesis of base metal occurrences in the mid-continent) as being related to an extension of a larger MVT system (Heyl A.V., 1982) or as related to diagenesis (Kutz K.B., 1989). For instance, fluid inclusion studies of quartz in the gossans by (Howe, 1981) (SS, 1981)and sulfur isotope studies of sulfides from Pb-Zn occurrences indicated that MVT processes occurred in the area. The second model relates mineralization could have formed during diagenesis. *Rose* (2005) used trace and major element geochemical signatures from the veined sulfides and host rocks to argue that the sulfides formed during diagenesis as a result of sulfidation of the host rock.

Mineralization throughout central and eastern Pennsylvania has been geochemically linked to MVT like processes. *Kesler and van der Pluijm* (1990) (the study identified similarity of Pb isotopic composition of ore from the Keystone mine and Friedensville to other Appalachian

MVT deposits), *Kesler* et al., 1995 (the study identified similarities of fluid inclusion evidence from the Schad and Keystone to other Appalachian MVT deposits), and (Appold M.S., 1995) (the study correlated sulfur isotope data for the Appalachian MVT and the data collected by *Howe* (1981) to indicate a common source of sulfur for these deposits) link Pb+ Zn mineralization in Pennsylvania to Appalachian MVT deposits. The results were interpreted to indicate that mineralizing fluids formed by a combination of connate and formation water brines most likely mobilized by Alleghanian orogenesis (between 280-310MA), with ore deposition analogous to Mississippi Valley-type Pb-Zn deposits (further described in (Oliver, 1986)).

This contribution explores the extent and overall impact of the previously unknown Eocene event. Previous studies identified and described Pb-Zn sulfide occurrences in Paleozoic strata in this area of the Valley and Ridge Province and several other locations in eastern Pennsylvania (Howe, 1981; Rose, 1999; Smith RC, 1977). Thus, to further understand the origin of epithermal sulfide deposits in the area and the extent of the younger mineralization, we measured the Re-Os contents of sulfides from 10 different mineral locations (Figure 1) spread throughout eastern to western Pennsylvania. The selection of the suite of deposits provides the following comparative analysis:

1. We chose both minor occurrences (Thompson mine, Keystone mine, and the Roosevelt mine) along with the historically largest Pb-Zn mines in Pennsylvania (Pequa, Friedensville, and Phoenixville).
2. The selected deposits span a large geographic region. The inclusion of eastern Pennsylvania sulfide occurrences allows for improved interpretation for the causes associated with the Eocene mineralization event.

Methods:

All samples were obtained from the collections at the Carnegie Museum of Natural History, Hillman Hall of minerals. No fresh sulfides from the historic mine sites were collected due to the chemical weathering of sulfides in a humid climate. The samples were hand –picked and powdered for analyses.

To characterize the mineralogy and chemistry of the samples, powdered X-ray diffraction (XRD) were performed on the sulfides. XRD analysis was conducted using a Scintag X-ray powder diffractometer. XRD scans were completed in slow, step-scan mode for precision analysis.

For Re-Os analysis, 0.7 to 2.1g sulfide mineral powders were completely dissolved by the carius tube method (Shirey S., 1995). Os and Re were separated by distillation and ion exchange chromatography, respectively (Mathur, 2000c). Samples were loaded into a thermal ionization mass spectrometer as salts (Creaser et al., 1991) and concentrations of Re and Os were determined by isotope dilution. Blank measurements for Re and Os ranged from 24-41 picograms and 0.4-1.2 picograms respectively, and the measured $^{187}Os/^{188}Os$ of the blank was 0.20 ± 0.02 throughout this study. All measurement errors have $2\sigma<0.5\%$; however, the greatest source of error in the measurement is the Os blank. Therefore, errors reported in Table 1 were calculated by varying the concentration of the Os blank between 1 and 2 picograms (further discussion in Mathur, 2000).

Results:

The XRD mineral identifications as well as the Re-Os concentration and isotope ratios are reported in table 1. The concentration of Re and Os range from 0.2- 2.3 part per billion (ppb) and 3-50 parts per trillion (ppt). A comparison of average concentration with 1 sigma errors of Re and Os in sphalerite (0.92 ± 0.80 ppb and 10 ± 9.2 ppt), pyrite (0.95 ± 0.9 ppb and 9 ± 6 ppt) and galena (1.1 ± 0.4 ppb and 33 ± 14 ppt) does not reveal any mineral phases contain higher concentrations of either element. The overall average concentrations of Re and Os are similar to those measured in porphyry copper deposits and other types of epithermal mineralization (Mathur, 2000a, b, 2002, 2005; Mathur et al., 2003).

Isochron plots of the data reveal 3 linear trends (figure 2). The calculated ages of the trends was determined using a conventional isochron plot with the ratios of daughter $^{187}Os/^{188}Os$ versus parent $^{187}Re/^{188}Os$ plots: $^{187}Os_m = {}^{187}Os/{}^{187}Os_i + {}^{187}Re_m(e^{\lambda t}-1)$; where: m= measured, λ= decay constant, t= time, i= initial (Ludwig, 2001). The decay constant we used for Re is 1.66×10^{-11} yr $^{-1}$ (Selby et al., 2007). Four samples from Phoenixville and Freidensville lie on a trend that yields a Model 1 age of 39 ± 4 Ma, $^{187}Os/^{188}Os_i$= 0.27± 0.03, MSWD= 1.3. Three samples from Keystone and Thompson lie on a trend that yields an age of 27 ± 4 Ma, $^{187}Os/^{188}Os_i$ = 0.05 ± 0.04, because three points does not possess statistical significance no MSWD is reported. Sixteen samples from Skytop, Pequa, Perkiomen, and Roosevelt lie on a trend that yields a Model 3 age of 32 ± 3 Ma, $^{187}Os/^{188}Os_i$ = 0.23 ± 0.03, MSWD= 5.3. Four of the sixteen from the previous trend are from Perkiomen and lie on a trend that yields a Model 1 age of 33 ± 4 Ma, $^{187}Os/^{188}Os_i$ = 0.19 ± 0.02, MSWD= 2.4.

The ages overlap within reported errors except the samples from the Keystone and Thompson mine, which lie slightly younger than the other trends on the isochron plot. The initial Os ratio is relatively consistent for all isochrons and possesses a significant non-radiogenic source for Os.

Discussion:

The Re-Os results from the sulfides serves to geochemically link the epithermal deposits to an Eocene age and relatively non-radiogenic sources of Os. Two aspects of the results tie the 10 analyzed occurrences (spanning over 200 Km radial distances to one another) to a similar event. First, multiple deposits that exist in western and eastern Pennsylvania (Pequa, Skytop, Roosevelt, and Perkiomen) fall along similar trends on the isochron diagram indicating a similar source fluid precipitated mineralization. Secondly, the calculated age and initial Os ratios overlap for Pequa, Skytop, Roosevelt, Perkiomen, Phoenixville and Friedensville. The overlap indicates that mineralization age and source could be identical. The Thompson and Keystone results do not overlap with the Eocene age and have an Os initial ratio that barely overlaps with chondritic mantle. Although inconsistent with the other 8 occurrences, the young age and non-radiogenic Os initial ratio clearly point to a process not related to MVT style mineralization.

Mathur et al. 2008 hypothesized the young mineralization event related to two possible causes, the Chesapeake Bay impact or Eocene volcanism present in southerly portions in the same geologic structure. The Eocene volcanics are labeled in figure 1. Because the deposits analyzed span a larger geographic region, the Eocene volcanism present in the West Virginian portions of the Appalachians (Southworth et al., 1993; Tso et al., 2004) could not be a cause for the mineralization in eastern Pennsylvania. No geologic relationships tie the Phoenixville, Friedensville, Perkiomen or Pequa with the alkalic volcanism present in West Virginia. Also noted on figure 1 are kimberlite occurrences in the area (Bikerman et al., 1997). Kimberlites normally follow lineaments and could theoretically cause mineralization, however the ages of known kimberlite activity do not coincide with the Re-Os ages determined here. Therefore, the young event that might have impacted mineralization in eastern Pennsylvania is the Chesapeake Bay impact. Tom's Canyon impact identified in the Atlantic Ocean 10's of kilometers east of New Jersey could also be important as it occurred at roughly the same time (Poag, 1998b).

Constraining the cause to the Chesapeake Bay impact is the most significant interpretation of the dataset. The identification by Wiley Poag (CW, 1997; Koeberl et al., 1996; Poag, 1996; Poag et al., 2009) of the fifth largest recognized meteoric impact crater centered on the town of Cape Charles on the eastern shore of tidewater Virginia represents a major tectonic event for the northeastern United States. Dating of the impact places it at 35±0.5 million years ago. Manifestations of this event have been reported as diverse as a tektite ejecta field for in the Atlantic Ocean and as the source for the locally distributed pebble jasper deposits in northeastern Virginia. One of the authors, as part of an FHWA SHRP program in 1985, identified echelon twinning in petrographic thin sections of the Townson gravel, a quartz aggregate use locally for concrete formulations. However, the majority of the published literature related to the local geology, sub-surface structure and groundwater of the impact site that were used in part to characterize the impact.

However, how the impact lead to the genesis of the epithermal sulfide veining event throughout Pennsylvania remains unclear. Links between ore deposits and impacts is not a new discovery. Many studies have demonstrated impacts such as Sudbury, Canada and the Vredefort dome in South Africa caused mineralization (Grieve, 1994; Grieve, 2005; Reimold et al., 2005). In fact, Grieve defined 3 general types of mineralization associated with meteor impacts: progenetic (ores existing before impact), syngenetic (formed during) and epigenetic (post impact). The isotopic and field evidence indicate that the mineralization analyzed here is epigenetic.

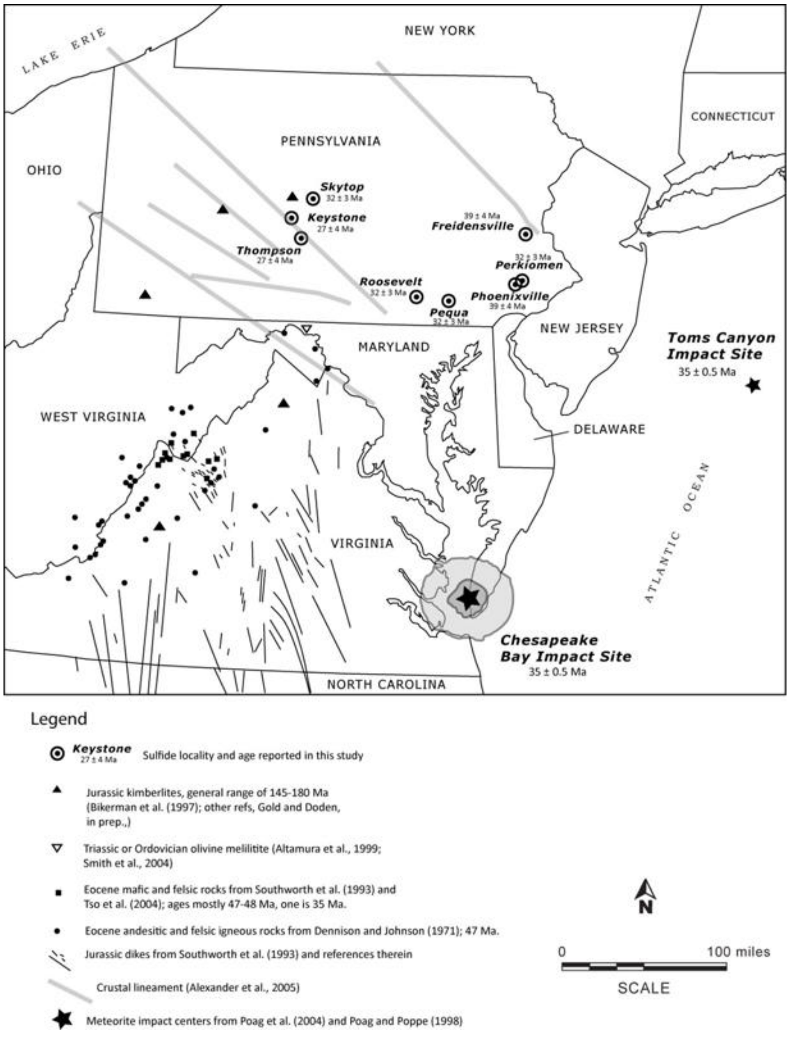
The exact processes that lead to mineralization could be related to 2 general mechanisms: hydrothermal convection cells driven by the heat of the impact or release of mantle fluids analogous to antipodal volcanism associated with impacts. For the hydrothermal convection cell model, breccias and ores associated with the large impacts of Sudbury and Vredefort dome are thought to be associated with hydrothermal flow of meteoric fluids associated with convective flow spanning up to 8Km (Pirajno, 2005). Consideration of only meteoric fluids would be difficult to model fluid flow over 100's of kilometers necessary to generate the epithermal mineralization evident in Pennsylvania. However, two factors associated with the Cheseapeake Bay impact may have allowed for the existence of a larger hydrothermal system. The Chesapeake impact occurred near or within seawater and the surrounding crust contains several overlapping joint and faults that would serve as ideal conduits for fluid flow. The preexisting fracture network is not clearly defined, however the Roosvelt, Thompson and Keystone sites are associated with the well documented and studied Tyrone/Mt. Union lineament (Gold, 1999) where mineralization has been recognized for nearly 200 years. Gold [1999] also identified an alignment of sulfide mineralization along a short lineament in Montgomery County which included the Perikoman mine. The Skytop deposit represents a juncture of a minor lineament and a recognized fault. Many other lineaments exist throughout the eastern and western Pennsylvania that could have served as conduits due to an orogenic history that has at least 4 (Grenville, Taconic, Acadian, Alleghanian) mountain building events impacting the area over the past billion years.

The second model of where the shock associated with this impact resulted in a hydraulically driven release of mantle-depth fluids, as evidenced by fluid inclusion temperatures of 400°C (Howe, 1981; Mathur et al 2008), which found their way to the surface through a discontinuous plumbing system of preexisting fractures in the crust. The nearly 0 ‰ per mil sulfur isotope data for Friedensville presented by Kesler and van der Plujm (1990) could be interpreted as a magmatic sulfur isotope signature. Continued analyses of other sulfide occurrences throughout the radial impact area will illuminate which pathways served as channels for the epithermal mineralization.

Aside from understanding processes associated with impacts of meteors, the identification of this large-scale mineralization in Pennsylvania associated with the Chesapeake Bay impact has long-range implications for future exploitation of economic resources as well as a direct impact on the civil transportation infrastructure. The I-99 example resulted in $80 million dollar expenditure by the Commonwealth of Pennsylvania to remediate the effects of acid rock drainage that was a direct consequence of the exposure and weathering of pyrite in this deposit. The full extent of the mineralization proposed in this hypothesis has not yet been fully delineated. Further, there is no reason to believe that the observed regional mineralization is limited just to Pennsylvania. Applying a systematic radius about the impact center and a line drawn from State College to Cape Charles would suggest the areas as far south as South Carolina and as far north as Connecticut including West Virginia, Virginia, Maryland, New York, New Jersey and Delaware should possess similar occurrences.

Mineral	Re (ppb)	Os (ppt)	$^{187}Re/^{188}Os$	error	$^{187}Os/^{188}Os$	error
pyrite	2.30	19	1142	103	0.53	0.03
sphalerite	0.33	17	90	8	0.29	0.02
galena	1.15	19	377	34	0.21	0.01
sphalerite	3.03	18	833	75	0.43	0.03
pyrite	0.65	11	365	33	0.41	0.02
sphalerite	1.10	5	574	52	0.47	0.03
sphalerite	0.41	5	371	33	0.41	0.02
pyrite	1.08	3	1906	172	0.23	0.01
pyrite	0.20	5	224	20	0.32	0.02
sphalerite	1.24	30	203	18	0.29	0.02
sphalerite	0.54	4	699	63	0.71	0.04
sphalerite	0.31	15	118	11	0.36	0.02
sphalerite	0.76	5	849	76	0.88	0.05
sphalerite	0.82	2	894	107	0.90	0.07
galena	1.48	30	250	23	0.32	0.02
sphalerite	0.65	3	1049	126	0.66	0.06
galena	0.43	21	106	10	0.29	0.02
pyrite	0.50	7	2312	208	0.91	0.05
galena	1.29	50	119	11	0.29	0.02
galena	1.20	46	110	10	0.27	0.02

Table 1. XRD Mineral Identificationa and Re-OS Concentration and Isotope Ratios in Pennsylvania


LAKE ERIE
NEW YORK
CONNECTICUT
PENNSYLVANIA
OHIO
Skytop
32 ± 3 Ma
Keystone
27 ± 4 Ma
Thompson
27 ± 4 Ma
39 ± 4 Ma
Freidensville
32 ± 3 Ma
Perkiomen
Roosevelt
32 ± 3 Ma
Pequa
32 ± 3 Ma
Phoenixville
39 ± 4 Ma
NEW JERSEY
MARYLAND
Toms Canyon
Impact Site
35 ± 0.5 Ma
WEST VIRGINIA
DELAWARE
ATLANTIC OCEAN
VIRGINIA
Chesapeake
Bay Impact Site
35 ± 0.5 Ma
NORTH CAROLINA
Legend
Keystone
27 ± 4 Ma
Sulfide locality and age reported in this study
Jurassic kimberlites, general range of 145-180 Ma (Bikerman et al. (1997); other refs, Gold and Doden, in prep.,)
Triassic or Ordovician olivine melilitite (Altamura et al., 1999; Smith et al., 2004)
Eocene mafic and felsic rocks from Southworth et al. (1993) and Tso et al. (2004); ages mostly 47-48 Ma, one is 35 Ma.
Eocene andesitic and felsic igneous rocks from Dennison and Johnson (1971); 47 Ma.
Jurassic dikes from Southworth et al. (1993) and references therein
Crustal lineament (Alexander et al., 2005)
Meteorite impact centers from Poag et al. (2004) and Poag and Poppe (1998)
N
0
100 miles
SCALE

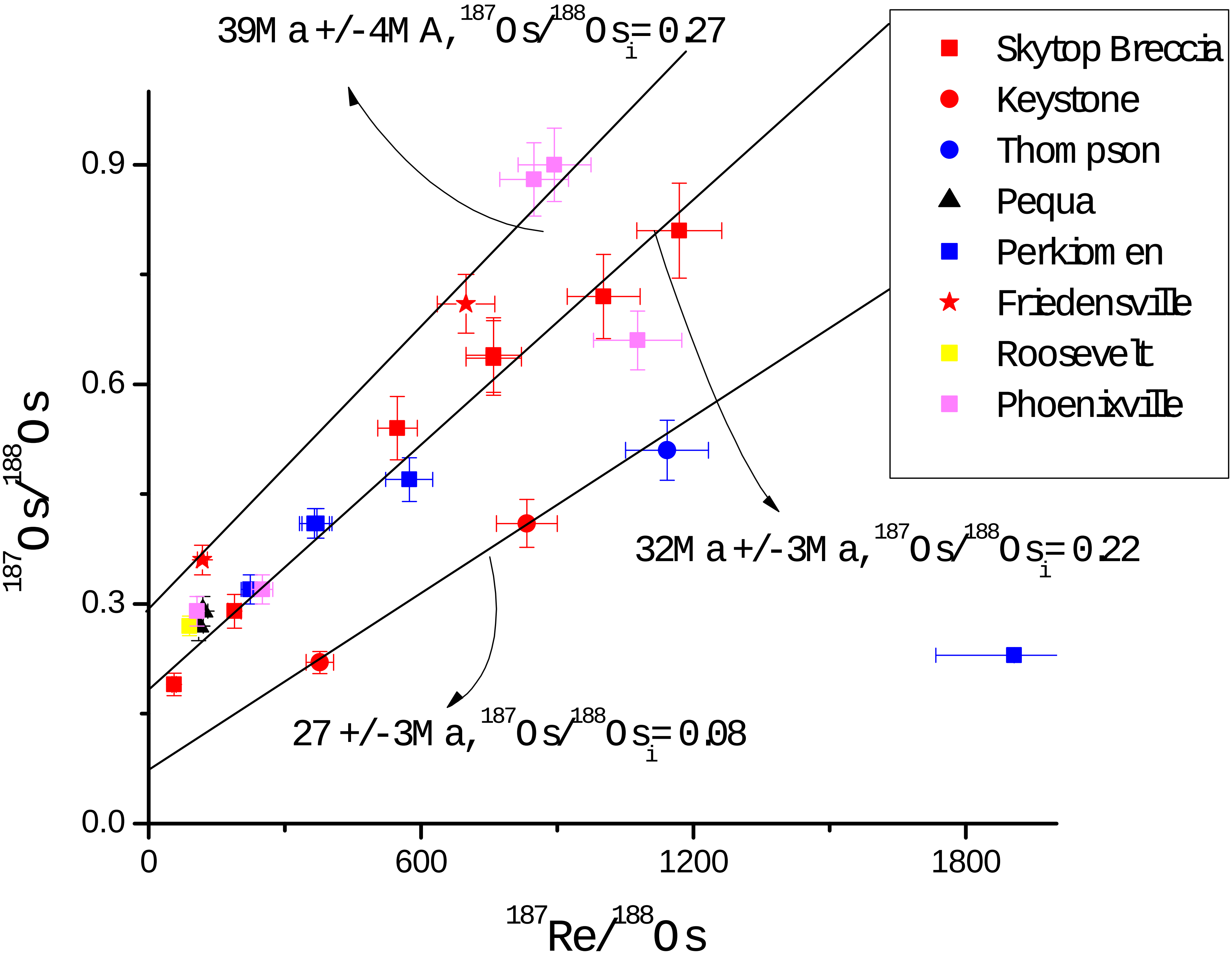

39Ma +/-4MA, ^{187}Os/^{188}Os$_i$=0.27
32Ma +/-3Ma, ^{187}Os/^{188}Os$_i$=0.22
27 +/-3Ma, ^{187}Os/^{188}Os$_i$=0.08
Skytop Breccia
Keystone
Thompson
Pequa
Perkiomen
Friedensville
Roosevelt
Phoenixville
^{187}Os/^{188}Os
0.0
0.3
0.6
0.9
^{187}Re/^{188}Os
0
600
1200
1800

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Figure captions:

Figure 1- Location map for the epithermal sulfide deposits analyzed. Also plotted are the Eocene volcanics of West Virginia, kimberlite occurrences, and major lineaments in Pennsylvania (data from (Altamura, 1999; Poag, 1998a; Poag, 2004; Smith, 2004; Tso et al., 2004).

Figure 2- Re-Os isochron plots of sulfide minerals from 10 deposits analyzed. Skytop data are Mathur et al. 2008.