Lead and Zinc in Central Pennsylvania

by

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INTRODUCTION

According to Miller, lead was mined in southern Sinking Valley as early as 1778. Miller (1924, p. 13-14), for example, notes:

> The first lead and zinc mines of Pennsylvania were operated in the Sinking Valley, Blair County, during the Revolutionary War. The Continental Army being in great need of lead for bullets, a party was sent to investigate some lead deposits said to be in the wilderness near Frankstown [Figure 1]. As a result of the examination General Daniel Roberdeau opened and worked some shallow mines in the southern end of Sinking Valley during 1778 and 1779. Several letters from General Roberdeau and others concerning these operations are in the Pennsylvania Archives, (First Series) especially in Vols. 6, 7, and 8. At one time 1,000 pounds of lead was sold to the State at $6.00 a pound in the depreciated currency of the period. It is not known when the mines closed but probably the operations were short-lived because of the expense of transporting materials for mining and smelting the ore, the maintenance of laborers in the Wilderness, as it was called, and the guards that were necessary on account of hostile Indians.

Reports about interactions between early colonists, Native Americans, and lead and silver abound. Eckman (1927), Price, L.F.D. (1947), and Loose (1972) fairly well document enslavement of Conestoga tribe Native Americans, to work lead-silver mines in the Pequea and Burnt Mills areas of Lancaster County.

A widespread genre of reports about lead in central Pennsylvania survived into the late 1960s. The basic theme of these fanciful stories is that an early colonist provides a service or rescue for a Native American. As a means of showing gratitude, the Native American leads the colonist blindfolded to an outcrop where pure natural lead can be cut or carved from the rock. The colonist collects for a day, is blindfolded again, and conducted safely back home. The crafty colonist, of course, isn't satisfied with a day's production and leaves red threads or breaks twigs on the way home. When he tries to relocate the lead deposit, he finds that the even craftier Native American has left scores of red threads or broken twigs in all directions (Richard Hammon, personal communication, 1973). Rather interestingly, some of those who passed on the genre were skilled amateur prospectors. Richard Hammon's father, Peter, *z.b.*, did some skilled lead prospecting at Silver Mine Knob, Huntingdon County, which wasn't rediscovered by geochemists until the late 1960s (Smith et al., 1971).

At $6.00 per pound, lead produced from the Fort Roberdeau area is likely the highest unit value mineral resource ever produced in central Pennsylvania. Interest in zinc was slower to develop but continued at least into the 1980s when a major corporation unsuccessfully attempted to lease the area of the old Soister Iron Mine (Smith, 1978, p. 120-124).

MINERALIZATION IN SINKING VALLEY

Minerals found in the Sinking Valley area include: the lead species galena, anglesite, cerussite, and jordanite; the zinc species sphalerite, hydrozincite, and smithsonite; and the gangue minerals barite and dolomite. It is generally thought that only galena was recovered in the area of Fort Roberdeau and only

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Figure 1. Early map of the Sinking Valley area NNE of Franks T and NW of Huntingdon. Forts Littleton, Loudon, Shirley, as well as a fort at Bedford shown, but Fort Roberdeau not yet built (Scull, 1770).

sphalerite in the Keystone Mine of northern Sinking Valley. Core drilling by the New Jersey Zinc Company yielded some zinc ore intercepts beneath the Keystone Mine (Noel Moebs, personal communication, circa 1960). Rose (1999), in his overview of lead and zinc in Pennsylvania, estimated a production from Sinking Valley of 3,500 tons of ore having a combined grade of 12% zinc plus lead.

Figure 2 (Smith, 1978, Figure 49) shows the locations of some of the then-known mines, prospects, and significant occurrences in southern Sinking Valley. Locations A through G were mines relocated as of 1976; whereas, H through N were reported, but unlocated. The Bellefonte Formation dolomite contact with the overlying Milroy Member of the Loysburg interbedded limestone and dolomite is approximated in Figure 2, but more accurately located in Plate 1 of Faill et al. (1989). Using the locations on Figure 2 and Faill et al.'s geology, the occurrences in southern Sinking Valley appear to be hosted in dolomites and dolomitic limestones from the upper Bellefonte Formation up to the Snyder Formation. In northern Sinking Valley in the Keystone Mine area, significant mineralization is located in Upper Cambrian Mines dolomite, Lower Ordovician Larke-Stonehenge dolomite-limestone, Nittany and Bellefonte dolomite at the Keystone Mine itself, limestones, possibly from as high as the Snyder or even Linden Hall formations.

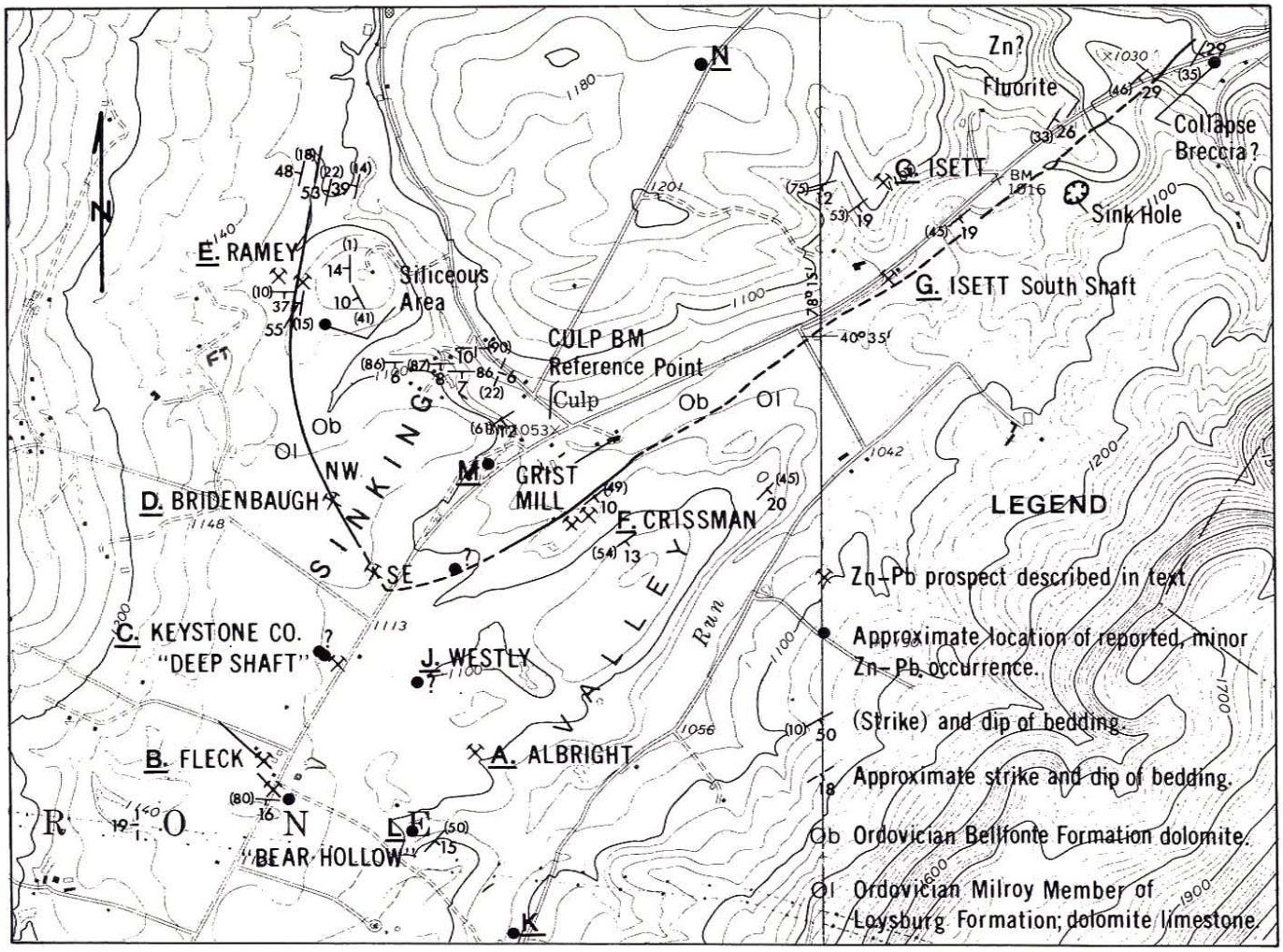


Figure 2. Zn-Pb mines, prospects, and significant occurrences in southern Sinking Valley from Smith (1978, Figure 49). See Plate 1 of Faill et al. (1989) for more accurate geology.

Except for a few, less brittle limestone beds observed in the Keystone Mine that were richly replaced by sphalerite and galena, nearly all of the ore in Sinking Valley is in open spaces in brittle fault breccias (A. W. Rose, personal communication, 1975). The vein-faults at the Fleck occurrences trend N48W, those at Bridenbaugh N30W and the Albright Mine may be on the extension of this latter fault. However, Reed

(1949, p. 5) found that at least one vein at the Albright Mine had a strike of nearly east and dipped 80 to 85 degrees to the north.

Based, in part, on the deformation of main stage galena from many prospects in central Pennsylvania, it can be reasonably hypothesized that such lead-zinc mineralization is a product of the Alleghanian orogeny. It is proposed herein that saline fluids that transported the metals were expelled from shaly units such as the Antes Member of the Reedsville Formation as a result of the Alleghanian orogeny. These fluids migrated along a northwest-trending zone (Smith et al., 1971) and other structures in upper Ordovician and lower Silurian clastics, and were deposited where the transporting saline fluids encountered pyrite of sedimentary origin in black shaly interbeds in the Tuscarora or in pyritic algal mats in the sabka facies of the Tonoloway Formation or possibly the Milroy Member of the Loysburg Formation. Where the fluids became oxidized or encountered sulfate-bearing ground water, barite also precipitated. This latter was very fortunate for early lead prospectors as barite associated with the galena in Southern Sinking Valley provided a nearly indestructible, readily recognized residue. Early settlers were used to the concept of "tracking" and it would have only been a small leap for them to have become Pennsylvania's earliest exploration geochemists.

From several other data sets, the maximum heating and subsequent cooling associated with the Alleghanian orogeny can be established. From laboratory studies of sphalerite and galena samples, the temperature of formation of lead and zinc mineralization can be determined. As shown below, an Alleghanian cooling curve can be combined with the temperature of formation of sulfides to estimate the time of formation of the lead and zinc deposits for Southern Sinking Valley and central Pennsylvania in general (Smith and Faill, 2000). Still other data sets establish a gentle, Mesozoic Thermal Pulse (MTP of Smith and Faill, 2000) that reheated the Sinking Valley area and far beyond, possibly to Montmorency Falls, Quebec. The MTP also helps explain the origin of zinc-lead-copper veins in southeastern Pennsylvania (Smith, 1977).

Logically, these same thermal histories and fluid movements also controlled oil and gas generation and migration. Indeed, it is possible for two blind men to hold different parts of the same elephant. Below follows a somewhat simplified version of a portion of Smith and Faill (2000) which they plan to update.

ALLEGHANIAN UNLOADING

In the past two decades, a wealth of data has been obtained in central Pennsylvania from thermal history indicators such as fission track annealing, vitrinite reflectivity, and various measures of hydrocarbon maturity. Michael L. Hulver's (1997) thesis, for example, is a *tour de force* compilation, recalibration, and interpretation of such data, and is highly recommended. However, for purposes of developing a simple model, those data may be overwhelming.

In contrast, Mary Roden Tice (in Way, Smith and Roden, 1986, and Roden and Miller, 1989) created an elegantly simple fission track data set for apatite crystals for the Ridge and Valley of Pennsylvania. These she separated from Tioga Ash Bed B using samples supplied by J. H. Way and the present author. These apatites were carefully collected from channel samples cut through the 390.0 +/- 0.5 Ma ($^{207}Pb/^{235}U$ date on monazite, Roden et al., 1990) Tioga Ash Bed B in central and eastern Pennsylvania. By making detailed, centimeter-scaled measurements of sections of the Tioga Ash Beds at many localities, Way and Smith found that positive identification of each bed was possible at many localities. Thus, they were assured of sampling the same ash bed at each locality. This identity was confirmed when George H. Shaw et al. (1992) analyzed splits of these same apatites and found them to have notably uniform ratios of La/Tb and Ce/Tb. Thus, Roden and Miller were able to work with a population of synchronously deposited apatite that would likely have minimal variation in composition.

Roden and Miller (1989) analyzed some of the Tioga Ash Bed B apatite samples for Cl. They found a small, but significant fraction: 0.2 for Cl/(Cl + F). Recent research published by Carlson et al. (1999)

included a study of Tioga Ash Bed B apatite from Old Port, PA, presumably from the same ash bed sampled by Way and Smith [confirmed, Ray A. Donalick, personal communication, 2002]. Carlson et al. (1999) found this apatite to contain 0.17 Cl atoms per formula unit and that it was the most resistant to annealing of nine normal apatites they studied (their Figure 3). Various studies have suggested that such moderately Cl-rich apatites are likely to anneal over geologic time at temperatures of ~120ºC. Thus, we now have a simple but elegant tool indicating when the Ridge and Valley had cooled to 120ºC following Late Alleghanian tectonism (circa 278 +/- 6 Ma, Smith and Faill, 1994). Except for areas near the thicker anthracite overthrusts (MacLachlan, 1985), Roden and Miller's Tioga B data show that much of the Ridge and Valley had cooled to 120ºC by the late Triassic. This yields a cooling rate of ~1.6ºC/Ma based on a maximum Alleghanian temperature of 200ºC at 278 Ma and cooling to 120ºC by 225 Ma. Roden's median Tioga Ash Bed B fission track age for samples distant from the anthracite region is 225 Ma, as was shown in Figure 1 of Way, Smith, and Roden (1986).

As inferred below, this cooling rate of ~1.6ºC/Ma likely continued until intrusion of the Quarryville Diabase, perhaps at ~ 205 +/- 5 Ma (?), at which time the temperature in the Ridge and Valley of central Pennsylvania might have been 90ºC. This would imply that normal fluorapatites in the Ridge and Valley would have ***first*** "set" at ~212 +/- 5 Ma.

A significant corollary of this cooling of much of the Ridge and Valley away from the anthracite region to 120ºC by 225 Ma is that the region had a cover of 4.2 km of sediment at 225 Ma. {Closure temperature (120ºC) minus current ambient temperature (15ºC) / geothermal gradient (25ºC/km) = ~ 4.2 km.} This appears to be consistent with Hulver (1997) who shows a maximum of 4 km of cover for this same region using a recalculated CAI (Figure 2.11) calibration and 4 km using coal volatile matter (Figure 3.09). It should also be noted that Lacazette and Engelder (1988) estimated an overburden thickness above the Reedsville shale of 4 km using fluid inclusion pressure estimates for an unspecified location.

Nearer the anthracite region, Roden obtained Tioga B apatite fission track ages as young as 152 Ma. These, as others (especially David B. MacLachlan, Pennsylvania Geological Survey) have suggested, likely represent the additional time required to erode the additional thickness of the anthracite overthrusts and, as discussed below, sediment eroded from the rebounded Mesozoic basins. This is consistent with the work of Orkan and Voight (1985), who reported a depth of ~ 5 km for the western anthracite region using H_2O-CH_4 fluid inclusions in quartz.

Far more complex patterns of Alleghanian unloading-cooling reported by others are believed, in part, to represent 1) variation in the compositions of the apatites studied (possibly including carbonate-fluorapatites) which would have different inherent annealing temperatures, 2) a residuum of significant dates of 141 Ma over a wide area [as discussed under The Mesozoic Thermal Pulse, below], and 3) the chance of a few samples being near hot springs related to deep circulation of meteoric water in a porous sandstone such as the Ridgeley.

SUGGESTED FURTHER ALLEGHANIAN UNLOADING RESEARCH

Carefully collected samples of apatite from other single ash beds should also yield useful, comparably smooth data. The ideal candidate may be Bentonite bed 13 of Smith et al. (1986) at the Union Furnace Section. Warren D. Huff (personal communication, 6/16/92) reports that B13 is likely the Deike K-bentonite of mid-continent terminology and that it is "loaded" with apatite and zircon at Union Furnace. Because Ordovician and Devonian sections are locally quite close to one another, a result of steep folding and faulting, cross calibration or at least comparison of data from the Ordovician and Devonian ash beds should be possible. Because Ordovician outcrops are more widespread and are frequently well exposed in commercial limestone quarries, an excellent data set should be obtainable. Further confirmation of the usefulness of apatites from a single ash bed might be possible by continuing study of the apatite and zircon-rich Bald Hill Bentonite C (Smith, et al., 1988) at the top of the Lower Devonian Helderberg Group. Such a study was begun by Roden and Miller (1989) who looked at two samples labeled "Kalkberg." The apatite in

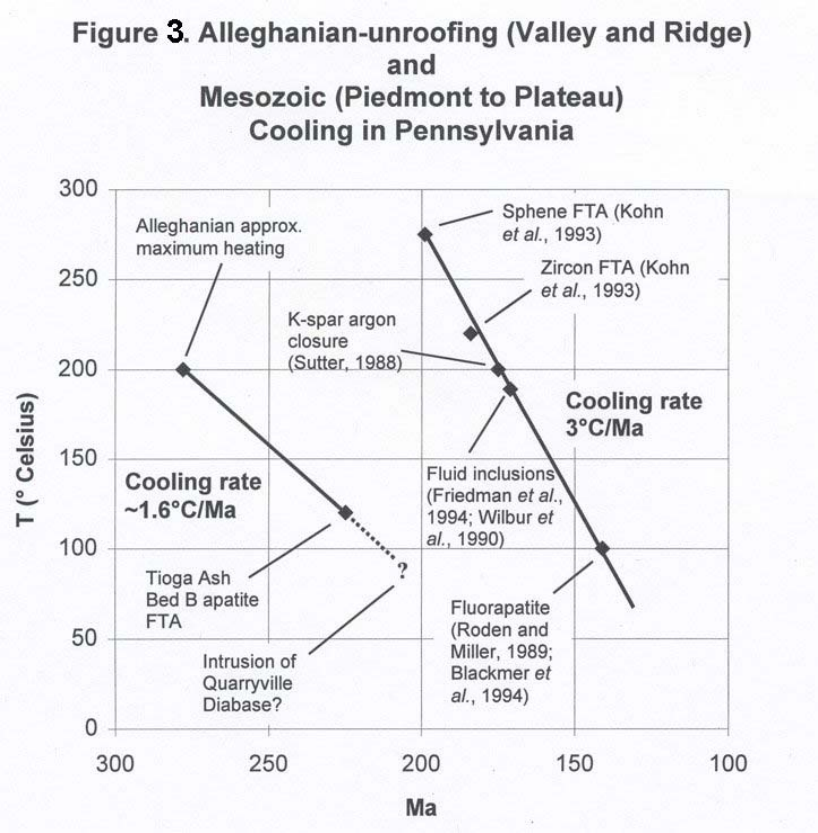
those was also found to have a Cl/Cl+F ratio of 0.2 and yielded apatite fission track ages of 203 and 246 Ma for a mean of 225 Ma. Now approximately 6 additional localities are known for Bald Hill Bentonite C and further study is encouraged. [See also Smith et al., 2003]

Roden and Wintsch (1992) tried to interpret fission tracks in zircons from some of the same Tioga Ash Bed B samples. However, based on the 200ºC Alleghanian maximum temperature for central Pennsylvania (vitrinite reflectivity, M.L. Hulver, 1997, Figure 3.20), it appears that the zircons from most of central Pennsylvania were never reheated to the 225 degrees needed to anneal zircon fission tracks after their original magmatic cooling. The exceptions occur nearer the anthracite overthrusts, where the sections were tectonically thickened more than elsewhere. For this area of zircon resetting, a two-point rate of Alleghanian cooling over the range of ~225º to 120ºC would be quite interesting.

MESOZOIC THERMAL PULSE

Just as the apatite FTA data of Roden provide a key to Alleghanian unloading, so FTA data on sphene and zircon, when combined with a few other small data sets, provide a relatively simple key to a Mesozoic Thermal Pulse (MTP) and rapid cooling. We envision this MTP as being caused by crustal thinning related to initiation of rifting. As always, the MTP and symptomatic diabase intrusions at ~ 200 Ma are the result of radiogenic heat released by decay of K, U, and Th in the mantle. This same heat flow attenuated the crust and provided for an elevated heat flow that extended well beyond the present boundaries of the Mesozoic basins.

The sphene and zircon FTA data were obtained for the Reading Prong, Newark Basin, and Piedmont of Pennsylvania and adjacent Maryland and Delaware by B. P. Kohn, M. E. Wagner, T. M. Lutz, and G. Organist (1993). They concluded that 1) there was a substantial MTP over their study area, 2) that cooling had progressed to a sphene-annealing temperature of ~275ºC by 199 Ma, 3) cooling had progressed to a zircon-annealing temperature of ~220ºC by 184 Ma, but that 4) away from Mesozoic diabase, heating never exceeded ~300ºC, based on lack of argon loss in biotite.



We concur with these conclusions, but note the even more widespread, normal fluorapatite FTA dates representing cooling to ~100ºC by 141 +/-3 Ma obtained by Roden and Miller (1989, 4 of 14 non-ash apatites) and by G. C. Blackmer, G. I. Omar, and D. P. Gold (1994, 8 of 29). As shown in Figure 3 (this paper), these dates fall on the sphene-zircon cooling trend following the MTP, but not on the trend for Alleghanian unroofing. Indeed, wide aerial distribution of the 141 Ma cooling milestone does not appear consistent with Alleghanian tectonic thickening. Thus, we are proposing that northwest of the failed Newark-Gettysburg Rift Basins, the MTP expressed itself as a broad, diffuse heating to less than ~120ºC (Cl-bearing Tioga B apatite not reset) but to more

than ~100ºC (normal fluorapatites reset). In a sense, this is a ~110ºC degree mirror image of the ~275 to <300ºC MTP found by Kohn et al. (1993) in the area between the failed and successful Mesozoic rifts.

Although frequently interpreted as a separate heating event, it seems reasonable to consider Sutter's (1988) 200ºC argon closure in potash feldspar at 175 Ma (Figure 3, this paper) as part of the cooling from the same MTP called upon by Kohn et al. (1993) to explain sphene and zircon FTA data and herein for fluorapatite FTA data. When all such data known to us are considered, a rapid, linear cooling at rate of 3ºC / Ma (Figure 3) seems appropriate for the period 200 Ma to 141 Ma.

Although preceded by the Triassic Quarryville Diabase, the Jurassic York Haven Diabase plus Rossville Diabase seem to represent the peak manifestations, but not the cause of the MTP. Three lateral equivalents of the York Haven Diabase were dated by Sutter (1988) using $^{40}Ar/^{39}Ar$, yielding a median of 201.2 +/- 1.3 Ma. Dunning and Hodych (1990) dated the Palisades Sill, a lateral equivalent of the York Haven Diabase, and obtained a median $^{206}Pb/^{238}U$ age of 201.2 Ma, probably +/- 1.0 Ma (avg. of 2 dates) for the best clear fragments of zircon. Similarly, they obtained an age of 201.0 +/- 1.0 (median of their 7 preferred analyses) for a small Rossville Diabase sheet (the D-263 body of Smith, 1973). The age of the York Haven Diabase is also well constrained by the position of the Jacksonwald basalt flow of that formation to a position 7 m above (Smith, et al., 1988) the *Corollina* zone used by Cornet (1977) to position the base of the Jurassic.

POSSIBLE AGES OF ZINC-LEAD MINERALIZATION BASED ON THERMAL MODEL

The best studied sphalerite and galena occurrences in the Ridge and Valley of central Pennsylvania occur in the Ordovician Bellefonte through Snyder formations and the uppermost Silurian Tuscarora Formation. Smith et al. (1971), Smith (1977), and Howe (1981) emphasized that much of this mineralization occurs in Alleghanian structures and that much main-stage mineralization is thoroughly deformed. (For example, galena from the Motel 22 occurrence, Huntingdon County, PA.) Howe (1981) also emphasized that the regionally consistent mineralization "…can be divided into six paragenetic stages, each separated by an episode of tectonic disturbance…." We would go so far as to speculate that the distinct stages of mineralization might be the result of tectonic realignment of the hydrothermal plumbing system, implying that there were six substantial pulses of tectonism over the course of mineralization. From this, is seems reasonable to assume, as others have done, that the mineralization is late Alleghanian. Combining this with the proposed cooling history (which seems to eliminate widespread Mesozoic reheating to 120ºC in central PA) and estimates of the temperature of formation of the sphalerites and galenas done by others, one can now approximate the age of the fluid migration and resulting mineralization. We suggest, however, that these are only approximations because the temperatures of hydrothermal systems might have exceeded regional temperatures at a given level if fluids came from great depth.

An example of how data on Alleghanian sphalerite-galena mineralization might be further interpreted and used to understand the Alleghanian orogeny itself follows. We will use one of Howe's (1981) two preferred intergrown sphalerite-deformed galena intergrowth samples, supplied as RS-04-07 from Albright occurrence A (Smith, 1977, p. 127) from southern Sinking Valley, Blair County. It yields a delta co-existing sphalerite-galena S^{34} temperature of formation of 137ºC and a sphalerite fluid inclusion temperature of 139.5ºC, perhaps suggesting little hydrostatic or lithostatic pressure. When plotted on Figure 3, this yields an estimated age of ~235 Ma. In general, Howe's sphalerite fluid inclusion temperatures range from 160ºC for the more southerly deposits studied in central Pennsylvania such as Woodbury (Smith, 1977, p 149-162) to 140ºC for the more northerly such as Milesburg Gap (Smith, 1977, p. 208-218). These would correspond to ages of ~260 and 240 Ma, respectively, suggesting that mineralization advanced from south to north. This is consistent with Stamatakos et al. (1996) paleomagnetic data suggesting fold development at 255+/-19 Ma and, indeed, hydrothermal solutions may have initiated the mineralization recorded by the

paleomagnetic data. If they were part of this system, hydrocarbons along the Allegheny Front might have been emplaced shortly thereafter, perhaps at ~225 Ma.

Likely, most of the significant Ridge and Valley sphalerite-galena occurrences were formed by one hydrothermal megasystem. This is suggested by the small, but systematic, variation in Howe's sphalerite fluid inclusion temperatures and by the fact that the vast majority of his sphalerites had uniform salinities of 24 to 25 weight percent equivalent NaCl. Likewise, Howe found that many sulfide minerals have delta S^{34} compositions close to +26 per mil. Recently, R. C. Smith and R. P. Nickelsen used this to establish a possible tie between the zinc-lead mineralization and a Tuscarora Formation tectonic breccia containing pyrite from the Mt. Pleasant Bank iron mine located at the intersection of the "late" Cowans Gap and Path Valley faults (Nickelsen, 1996, p. 8). They predicted 27 per mil for pyrites from the Hares Valley Zn-Pb district and Mt. Pleasant Bank, and obtained values of 25.6 and 26.6 delta S^{34}, respectively, suggesting the possibility of a common source fluid. Kessler et al. (1994) studied the same suite of Bellefonte through Snyder and Tuscarora-hosted sphalerite and galena samples supplied by Smith and found an extremely small spread of $^{206}Pb/^{204}Pb$ isotopes clustered at about 18.55, again suggesting a common hydrothermal system for deposits in the two different host rocks. In this study of paleoaquifers, Kessler et al. called this "…significant cross-formational flow."

Jeanne Passante Lawler (1981) studied fluid inclusions in sphalerites provided by B.C.S. II from the three Zn-Pb districts in the Newark Basin of eastern Pennsylvania. These are the Audubon, New Galena, and Phoenixville Districts (Smith, 1977, p. 226-270), each hosted in different units. (The only diabase observed by the senior author at any of these was irrelevant Catoctin equivalent metadiabase observed on a dump and in cores from one of the Phoenixville District mines, Smith and Barnes, 1994.) She found that most inclusions in sphalerite contained fluids having 11 to 16 equivalent weight percent NaCl, with the higher percentages from New Galena. The fluid inclusion homogenization temperatures for the most typical sphalerite samples from Phoenixville ranged from 175 to 185ºC, those from Audubon ranged from 160 to 170ºC, and those from New Galena from 135 to 145ºC. This cooling from south to north may also represent the direction of fluid migration. Using our Mesozoic cooling curve (Figure 3, this paper) and Lawler's homogenization temperatures, then typical sphalerites from Phoenixville appear to have formed at ~167 Ma, those from Audubon at ~ 163 Ma, and those from New Galena at ~155 Ma. Lawler calculated hydrostatic pressure corrections, but they do not seem to be appropriate for the uplifted southern portion of the Newark Basin.

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