

FINAL TECHNICAL REPORT

Comparative Analysis of Fluid Inclusion Geochemistries from World-Class and Small-Scale Zn-Pb Deposits in the Ozark Plateau using Laser Ablation ICP-MS and Raman Spectroscopy

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Abstract

Fluid inclusions hosted by sphalerite and dolomite and quartz gangue from the Southeast Missouri, Tri-State, and Northern Arkansas Mississippi Valley-type (MVT) districts of the Ozark Plateau of the central U.S. were analyzed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and Raman spectroscopy. The goals of the study were to characterize the chemical composition of fluids involved in mineralization. In particular, the study aimed to determine the ore metal and sulfur concentration, pH, and redox potential of the mineralizing fluids, to identify the mechanisms that caused the precipitation of the ores, and to determine if any compositional differences existed between fluids that deposited giant MVT districts like Southeast Missouri and Tri-State compared to those that deposited a small district like Northern Arkansas.

The results of the study showed that the MVT deposits in each district were deposited from brines with similar overall geochemistry dominated by the cations, Na, Ca, K, Mg, Sr, and Ba. Each of the three districts had a population of sphalerite-hosted fluid inclusions that was anomalously Pb and Cu rich relative to typical sedimentary basinal brines, with concentrations on the orders of 100's to 1000's of ppm. Gangue mineral-hosted fluid inclusions did not have ore metal concentrations above the detection limits of 1's to 10's of ppm. These results point to the invasion of a metal rich brine during the time of sulfide mineral precipitation. The high metal concentrations would have prevented simultaneous transport of large concentrations of sulfide. Thus, MVT ore deposition is more likely to have been caused by mixing of a metal rich fluid with a H₂S rich fluid or mixing of a fluid carrying metals and sulfate with another fluid rich in a reductant like methane. A constraint on the relative likelihood of these two mechanisms may come from the gas geochemistry of the fluid inclusions. Methane is prevalent in fluid inclusions in both sphalerite and gangue minerals from all three districts suggesting reducing log f_{O_2} values in the range of about -54 and -55, whereas H₂S is present only in sphalerite-hosted fluid inclusions. This suggests that sulfur was transported with metals, most likely in the form of sulfate, which was reduced to sulfide, perhaps by methane, in the reducing environment encountered in the MVT districts, triggering sulfide mineral precipitation.

Statement of Problem

Mississippi Valley-type (MVT) deposits represent some of the greatest enrichments of zinc and lead in the Earth's crust, exceeding average crustal concentrations by as much as three orders of magnitude in deposits up to hundreds of millions of tons in size. Several decades of research has produced a general model for MVT ore formation involving precipitation from sedimentary brines that commonly were set in motion by tectonic activity. However, many important details of MVT ore formation have remained unclear, such as exactly what causes the ores to precipitate from the brines. Possible precipitation mechanisms that have been proposed can be grouped into three categories (Sverjensky, 1986):

(1) Reduced sulfur model: Ore metals and sulfide are transported together in solution with sulfide mineral precipitation caused by cooling, dilution, or pH increase.

(2) Sulfate reduction model: Ore metals are transported in solution with sulfate, which is reduced to sulfide at the site of ore deposition most likely by organic matter.

(3) Mixing model: Ore metals and sulfide are transported in separate fluids that mix at the site of ore deposition.

Some of the most powerful clues to the answer to the precipitation mechanism question lie in the ore fluid composition. The major element composition and temperature of MVT ore fluids have long been known. However, other ore fluid characteristics have been much less certain. Chief among these are the ore metal content, the sulfur content, the pH, and the redox potential. Knowledge of these ore fluid characteristics will help answer other fundamental question regarding MVT ore genesis, such as whether MVT ore fluids are anomalous in any respects compared to typical sedimentary brines, and to what extent ore fluid chemistry affects MVT deposit size.

The Ozark Plateau of the Central U.S. is perhaps the world's foremost province of MVT mineralization (Fig. 1). The province contains the world's two largest MVT districts—the Southeast Missouri and Tri-State districts, three much smaller but still formerly commercially significant districts called the Northern Arkansas, Central Missouri, and Washington County districts, and numerous subeconomic occurrences of MVT mineralization. Located within the Mississippi River watershed, the Ozark MVT deposits are among the original defining examples of the MVT deposit class. Thus, research findings for the Ozark deposits have broad implications for the MVT deposit class as a whole.

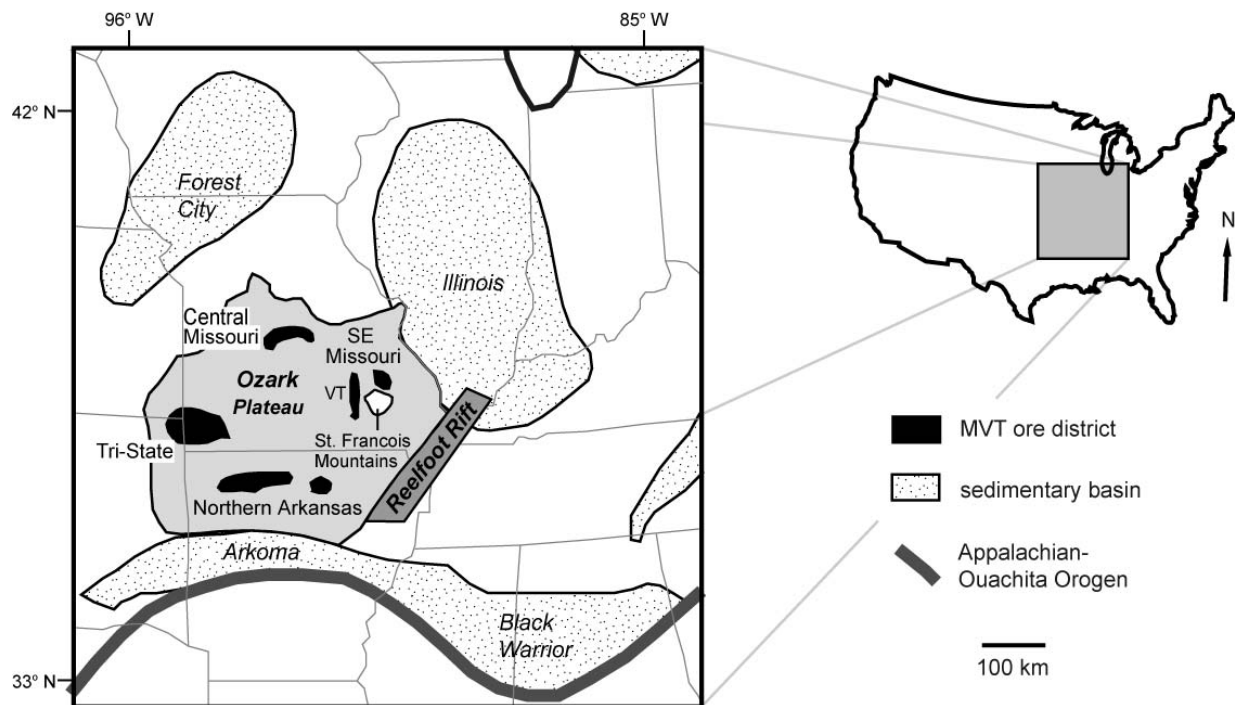


Figure 1. Map showing the location of the major MVT districts of the Ozark Plateau in relation to other major nearby geologic features (after Appold and Garven, 1999). The Viburnum Trend of the Southeast Missouri district is denoted by "VT."

Objectives

The principal objectives of this research project were to answer the following questions:

- What was the composition of the fluids involved in MVT mineralization? In particular, what was their ore metal content?
- What was the sulfur content of the mineralizing fluids?
- What were the pH and redox potential of the mineralizing fluids?
- What precipitation mechanisms were most important in forming the Ozark MVT deposits?
- Did the fluids that formed giant districts like Southeast Missouri and Tri-State differ significantly in composition from those that formed small districts like Northern Arkansas?

These objectives were pursued primarily through the analysis of fluid inclusions using microthermometry, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and Raman spectroscopy.

Methodology

Fluid inclusions were studied by preparing doubly polished thin sections from a variety of ore sample types and locations in the Southeast Missouri, Tri-State, and Northern Arkansas districts. Sample locations and their corresponding identification codes are listed in Appendix I. Most of the samples in this study were collected by the principal investigator (PI) and University of Missouri—Columbia (MU) doctoral student, Zachary Wenz, whom the PI is mentoring and for whom this project constitutes a significant portion of his dissertation research. Although neither the Northern Arkansas nor the Tri-State district is actively being mined, suitable samples for study were readily found in the field. Most of the Tri-State mines are located well below the water table and are now flooded with water so that they are not easily accessible. However, many of the smaller mines have coarse tailings piles adjacent to the entrance shafts, offering sample material that is probably no more than a few tens of meters removed from its source. The topographic relief in the Northern Arkansas district is generally much greater than that in the Tri-State district and much of the mineralization occurs in shallow mines above the water table or in outcrop so that mineralization commonly could be sampled in situ. The Southeast Missouri district is still actively being mined and most of the mineralization lies in the subsurface on property of the Doe Run mining company. Samples for this study were obtained by the PI on Doe Run mine field trips and as donations from Dr. Kevin Shelton, Professor of Geological Sciences at MU, and from George Moellering, Chief Mine Geologist at Doe Run.

Doubly polished sections were prepared at low temperatures using water as a lubricant to prevent fluid inclusion stretching. In order to see clearly the abundant fluid inclusions typically present in dolomite, thin sections that consisted predominantly of dolomite were prepared to relatively

low thicknesses of 30-60 μm . Thin sections consisting predominantly of sphalerite were prepared to thicknesses of 80-120 μm . Fluid inclusion origin was based on the criteria of Goldstein and Reynolds (1994). Fluid inclusion microthermometry was performed using a LinkamTM THGMS 600 heating-cooling stage at MU. Measurement precision was $\pm 0.1^\circ\text{C}$ and estimated accuracy was $\pm 0.2^\circ\text{C}$. Raman microprobe analysis was carried out using a JY Horiba LabRam HR800 spectrometer coupled to a LaserPhysics Reliant 100S-514 nm argon laser at the Virginia Polytechnic Institute and State University (VPI) Department of Geoscience. Elemental concentrations of inclusion fluids were measured using an Agilent 7500ce quadrupole ICP-MS coupled to a GeolasPro Excimer 193 nm ArF laser ablation at the VPI Department of Geoscience.

Reduction of the LA-ICP-MS fluid inclusion data was carried out using the ExLAM software of Zacharias and Wilkinson (2007) and the AMS 6.1.1 software of Mutchler et al. (2008). Calculation of absolute elemental concentrations in fluid inclusions was accomplished using Na as an internal standard. An independent determination of Na concentration in the fluid inclusions was obtained from the last-ice-melting temperature, which was converted to equivalent weight percent NaCl using the equation of state of Bodnar (1993). Equivalent weight percent NaCl was then converted to actual weight percent NaCl using the algorithm of Heinrich et al. (2003).

After completion of the LA-ICP-MS analyses, the paragenetic stage of the dolomite-hosted fluid inclusions from Southeast Missouri was determined by cathodoluminescence microscopy using a Nuclide Corporation cathode luminoscope in the Department of Geology and Geophysics at the Missouri University of Science and Technology.

Results

The present study generated a total of 358 LA-ICP-MS analyses (documented in Appendix II) and hundreds of Raman microprobe analyses of fluid inclusions hosted by sphalerite, dolomite, and quartz from the Tri-State, Northern Arkansas, and Southeast Missouri districts. In addition, the study generated 374 LA-ICP-MS mineral matrix analyses of sphalerite from these three districts (Appendix III). Results are discussed below in reference to the principal objectives of the project. Additional details are presented in a manuscript by Appold and Wenz currently under review with *Economic Geology*, and in a manuscript in preparation by Wenz and Appold to be submitted to the *American Journal of Science*.

- **What was the composition of the fluids involved in MVT mineralization? In particular, what was their ore metal content?**

The elemental composition of MVT ore fluids has long been recognized to resemble that of modern sedimentary brines. However, this conclusion is based largely on bulk crush leachate analyses of MVT ore minerals that typically produce mixtures of unknown proportions of primary and secondary fluid inclusions, and are susceptible to contamination by the mineral matrix. LA-ICP-MS offers an opportunity for more rigorous characterization of MVT ore fluid

composition by analyzing individual fluid inclusions whose origin can be determined petrographically.

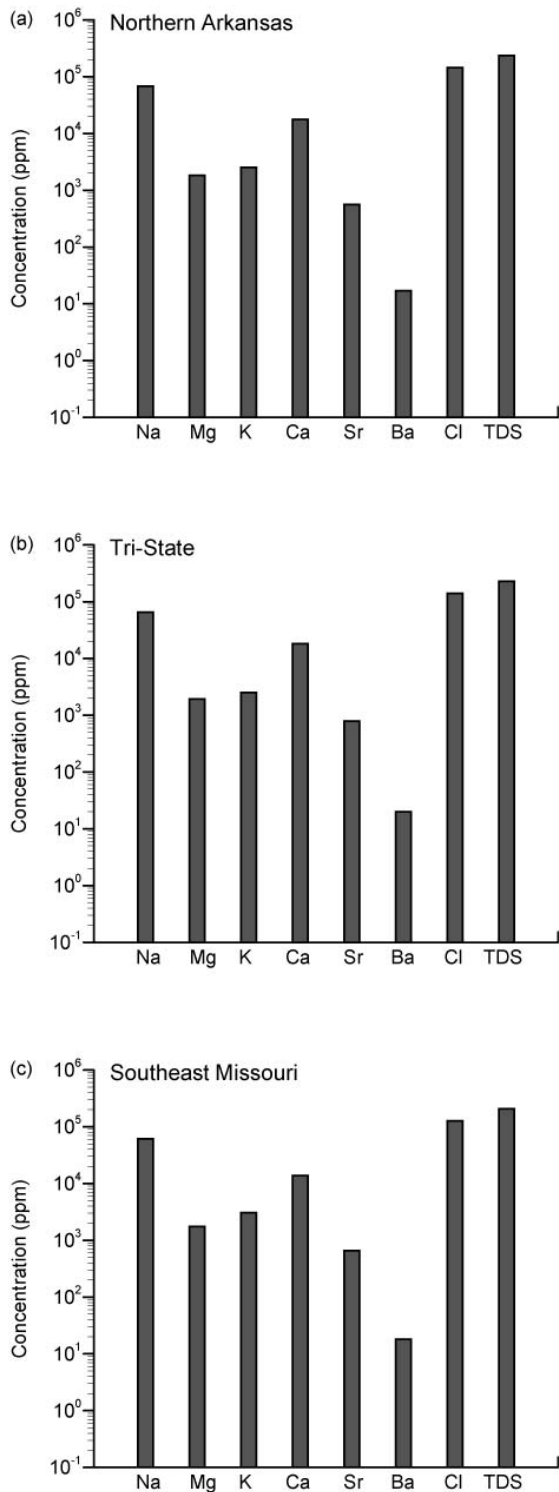


Figure 2. Major element and TDS concentrations of sphalerite-hosted fluid inclusions from the (a) Northern Arkansas, (b) Tri-State, and (c) Southeast Missouri districts.

Figure 2 shows bar graphs of the average non-ore metal and total dissolved solids (TDS) concentrations of sphalerite-hosted fluid inclusions from the Northern Arkansas, Tri-State, and Southeast Missouri districts. The graphs show that the three districts have very similar non-ore metal compositions. Sodium is the most abundant cation in solution, followed by Ca, K, Mg, Sr, and Ba. Chloride was not measured directly but was computed by mass balance assuming that it is the only anion in solution. (In typical sedimentary brines, chloride accounts for at least 95% of the mass of anions in solution—Hanor, 1994.) Despite the overall similarities in composition, some noticeable differences exist. Southeast Missouri fluid inclusions on average are enriched in K and depleted in Ca relative to Northern Arkansas and Tri-State fluid inclusions, and Tri-State fluid inclusions are enriched in Sr relative to the other two districts.

The concentrations of the ore metals vary widely in the fluid inclusions but were highest in sphalerite-hosted fluid inclusions. Zinc could not be measured in sphalerite-hosted fluid inclusions because it is present in the sphalerite matrix in concentrations that are too high to allow the aqueous signal to be resolved in the LA-ICP-MS spectra. Lead and Cu are commonly present in significant concentrations in the sphalerite matrix. Nonetheless, Pb and to a lesser extent Cu were measurable in some fluid inclusion assemblages (FIA's). Though most fluid inclusions had Cu concentrations below the detection limit of 10's to 100's of ppm, some had very high concentrations—up to 3200 ppm in Northern Arkansas and up to 1700 ppm in Tri-State. A smaller suite of analyses from Southeast Missouri did not yield any quantifiable Cu concentrations in fluid

inclusions. As for Cu, though most fluid inclusions had Pb concentrations below the detection limit of 1's to 10's of ppm, some had very high concentrations—up to 3200 ppm in Northern Arkansas, up to 1200 ppm in Tri-State, and up to 340 ppm in Southeast Missouri. It is quite possible that higher Pb concentrations exist in some Southeast Missouri fluid inclusions, but the sphalerite from Southeast Missouri has the highest matrix Pb content of the three districts, which overwhelmed the aqueous Pb signal of many fluid inclusion analyses. This high matrix Pb content, however, argues indirectly for a high Pb concentration in the ore fluid.

- **What was the sulfur content of the mineralizing fluids?**

The concentration of ore metals and the mechanism for their precipitation is strongly dependent on the concentration and oxidation state of sulfur in the ore fluid. Thus, determination of the form and concentration of sulfur was one of the goals of the project. Sulfur is not easily quantified by LA-ICP-MS because of mass interferences with the abundant oxygen dimer. However, Raman spectroscopy is routinely used to identify sulfur species in aqueous solution and in the vapor phase of fluid inclusions.

A thorough survey of Ozark MVT fluid inclusions using Raman microprobe analysis showed H₂S to be a common constituent of sphalerite-hosted fluid inclusions. The concentration of H₂S in the fluid inclusions was not determined because of the experimental challenges in making synthetic H₂S-bearing fluid inclusions to be used as calibration standards, for which the PI does not have suitable laboratory infrastructure. Inquiries made by the PI to numerous experimental geochemists who work with H₂S did not reveal any sources from which synthetic H₂S-bearing fluid inclusion calibration standards could be procured.

Raman microprobe analysis also showed none of the fluid inclusions hosted by any MVT mineral to contain detectable concentrations of sulfate. Because sulfate does not exist as a gas and is not toxic, synthetic fluid inclusion standards could readily be produced. The calibration standards were produced by forming solutions containing variable concentrations of Na₂SO₄ saturated with respect to halite at about 90° C. Upon cooling, halite crystals precipitated, trapping some of the ambient solution as fluid inclusions. Systematic Raman microprobe analysis of the fluid inclusions showed the detection limit for sulfate to be about 5×10^{-3} molal (Fig. 3). Thus, Ozark MVT ore fluids can be inferred to have had sulfate concentrations less than this value.

- **What were the pH and redox potential of the mineralizing fluids?**

The pH of a fluid inclusion could in theory be determined if the concentrations of two aqueous species of an element in solution, e.g. SO₄²⁻ and HSO₄⁻ or H₂CO₃ and HCO₃⁻, exist in sufficient concentrations to be quantified. No species pairs were found in sufficient concentrations to allow a pH determination to be made. However, an estimate of redox potential could be made from the concentration of methane, which Raman analysis showed to be a principal constituent of the vapor bubbles of many fluid inclusions in sphalerite, dolomite, and quartz. Redox potential estimates have so far only been made for sphalerite-hosted fluid inclusions from the Southeast Missouri district. Following the procedure of Lin et al. (2007), the partial pressure of methane in the fluid inclusion vapor bubble at room temperature could be determined from the

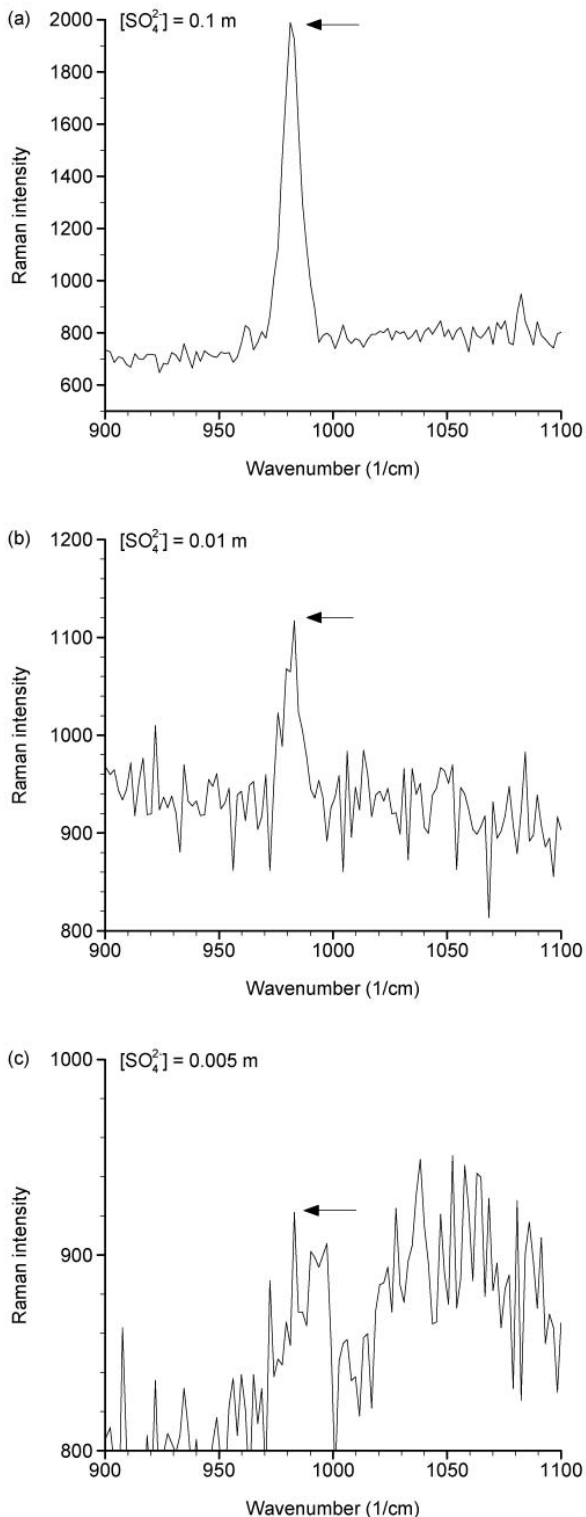


Figure 3. Raman spectra for sulfate in synthetic fluid inclusions in halite. The Raman peak for sulfate occurs at a wave number of about 983 cm^{-1} , indicated by the arrow, and ceases to be detectable below concentrations of about 0.005 molal.

magnitude of the shift of the symmetric stretching band, which moves to lower wave number with increasing pressure. Assuming that all of the methane was miscible at the time of fluid inclusion entrapment, its aqueous concentration can be determined from the $\text{H}_2\text{O-NaCl-CH}_4$ equation of state of Duan and Mao (2006) and homogenization temperature using an iterative mass balance calculation (R. J. Bodnar, personal communication). Thus, the dissolved methane concentration of ore fluid during the time of sphalerite precipitation in Southeast Missouri appears to have been about 0.02 molal.

This methane concentration can be used to constrain the redox conditions during sphalerite precipitation. Figure 4 shows a plot of log methane solubility as a function of pH and oxygen fugacity, calculated using Geochemist's Workbench (Bethke, 2004) for an average Southeast Missouri fluid composition where total carbon content was governed by saturation with respect to dolomite. For a pH between 4 and 5, a likely range for MVT fluids (Leach & Sangster, 1993), log f_{O_2} values ranging between about -54 and -55 would be predicted, causing sulfur to exist predominantly in the form of sulfide.

- **What precipitation mechanisms were most important in forming the Ozark MVT deposits?**

The fluid composition data obtained in this research has important implications for possible ore precipitation mechanisms for the Ozark MVT deposits. First, the relatively high Pb concentrations of sphalerite-hosted fluid inclusions make it unlikely, at least in the case of Tri-State and Southeast Missouri, that ore metals were transported together with sulfide in solution, as the sulfide concentration would have been

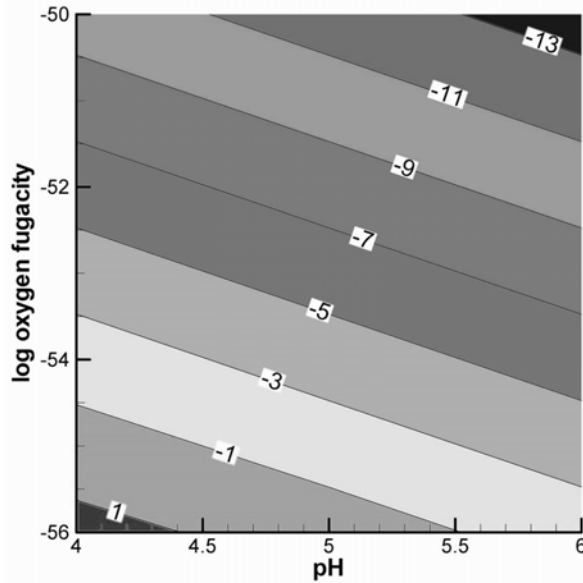


Figure 4. Contour plot of methane solubility as a function of pH and $\log f_{O_2}$ for an average Southeast Missouri fluid composition where total carbon content was governed by saturation with respect to dolomite.

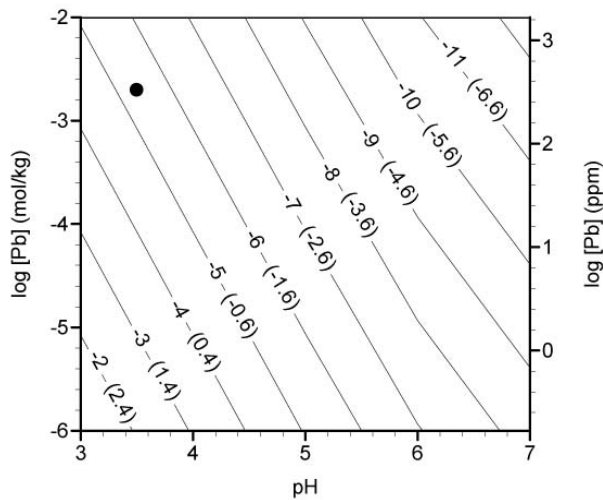


Figure 5. Contour plot of the log molal total sulfide concentration in equilibrium with galena as a function of pH and Pb concentration in a 4 molal chloride solution at 100° C and $\log f_{O_2} = -60$ from Stoffell et al. (2008). The contour values shown in parentheses represent log ppm total sulfide concentrations. The dark circle near the top left corner of the plot represents the total concentration of sulfide (4×10^{-6} molal) that could coexist in solution with 340 ppm Pb (the maximum concentration measured in fluid inclusions) at a pH of 3.5 (a likely minimum for basinal brines—Hanor, 1994).

too low to allow the observed masses of ore to have been deposited within geologically reasonable periods of time.

For example, Figure 5 shows the concentration of total sulfide in equilibrium with galena as a function of pH and Pb concentration in a 4 molal chloride solution at 100° C. The figure shows that a fluid carrying 340 ppm Pb, the maximum value found from the Southeast Missouri analyses, could only carry about 4×10^{-6} molal sulfide in solution at a pH of 3.5, near the lower limit found in typical sedimentary brines (Hanor, 1994). It should be noted that the Pb concentration of the ore fluid could have been even higher than 340 ppm. The wide range of Pb concentrations in the fluid inclusions suggests some type of fluid mixing, which in the present case could have caused dilution or a pH increase of the ore fluid. Thus, the fluid inclusions would represent mixtures of varying proportions of at least two end member fluids, one of which was Pb rich and whose Pb concentration must have been at least as high as the highest concentration found in the mixture.

The low sulfide concentration able to coexist with the high Pb concentration then becomes a strong limiting factor for ore formation. Figure 6 shows a mass balance calculation representing the length of time needed to deposit all of the Viburnum Trend's 1.1×10^{11} moles of sulfur bonded to the same number of moles of Pb (equivalent to about 25 million tons) in galena (Ohle and Gerdemann, 1989) as a function of aqueous sulfur concentration and Darcy velocity. As in Appold and Garven (1999), the calculation assumes a cross sectional area of flow of 10 km \times 100 m, the approximate width and thickness of the St. Francois aquifer, which consists of the Lamotte Sandstone and the Bonneterre Dolomite. The most likely transport conditions are depicted by the lower gray shaded box, which could in theory extend beyond the left and bottom boundaries of the box, but would then lead to durations for ore

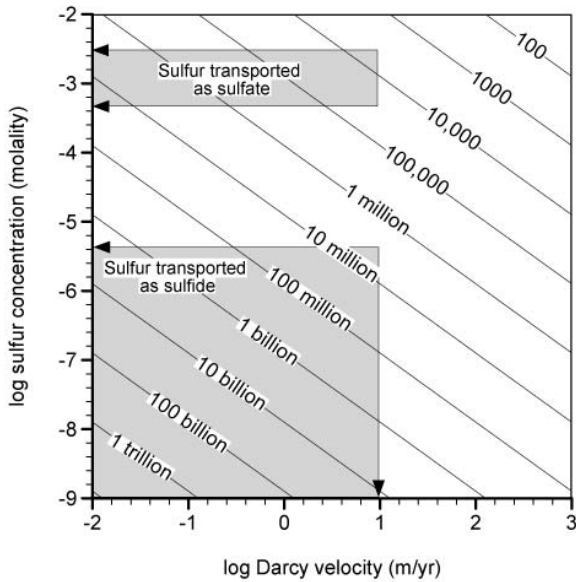


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deposition that substantially exceed the age of the Earth. The most optimal transport conditions occur at the top right corner of the lower shaded box, which corresponds to an assumed maximum Darcy velocity of about 10 m/yr (Appold and Garven, 1999) and the maximum sulfide concentration able to be transported with 340 ppm Pb at 100°C at a pH minimum of 3.5. Under these conditions, the Viburnum Trend ores could have been deposited in a still geologically reasonable time of several million years. However, for every 0.5 unit increase in pH and for every order of magnitude decrease in groundwater velocity and increase in aqueous Pb concentration, the length of time needed for ore formation increases by one order of magnitude. Thus, simultaneous transport of sulfide with Pb at concentrations of hundreds of ppm would require conditions near the limits of what is observed in nature.

It should also be noted that if sulfur was transported with Pb in the form of sulfate at concentrations of 3×10^{-3} to 5×10^{-4} mol/kg governed by barite saturation as noted above, then if all of the sulfate was reduced to sulfide, the Viburnum Trend's sulfur could easily have been deposited in a geological reasonable period of time, even at relatively low groundwater flow rates (see upper shaded box of Figure 6). Whether redox conditions would have allowed sulfate to exist at such concentrations is not clear. Redox conditions during sphalerite precipitation in Southeast Missouri would strongly have favored sulfide over sulfate. However, this could represent conditions caused by mixing and does not rule out the possibility that a metal-rich fluid was oxidizing with sulfur predominantly in the form of sulfate prior to mixing. Methane-rich fluid inclusions have been identified in gangue minerals from Ozark MVT deposits, suggesting that conditions were generally reducing throughout the time of MVT ore deposition. Thus, it is possible that an oxidizing, metal-rich,

sulfate-bearing fluid entered a reducing, methane-rich environment in the MVT ore districts, causing sulfate to be converted to sulfide and thus triggering the precipitation of the sulfide ore minerals. It is also possible that the metal-rich fluid was reducing and entered another reducing environment in the MVT ore districts that was enriched in H₂S, thus triggering sulfide ore mineral precipitation. However, the restriction of detectable H₂S to sphalerite-hosted fluid inclusions suggests that sulfur entered the district with metals, and thus would favor the sulfate reduction model.

- **Did the fluids that formed giant districts like Southeast Missouri and Tri-State differ significantly in composition from those that formed small districts like Northern Arkansas?**

Fluid inclusions hosted by sphalerite offer the most direct means for comparing ore fluid chemistry among the three districts. Sphalerite in all three districts appears to have precipitated from Na-Ca-K-Mg-Cl brines with TDS concentrations between 208,000 and 235,000 ppm (Fig. 2). Fluid inclusions from Northern Arkansas on average had the highest concentrations, followed by Tri-State and Southeast Missouri. Atomic Ca/Mg ratios in sphalerite-hosted fluid inclusions average about 5.5 in all three districts (Fig. 7), which is well below the maximum of 34 needed for dolomitization (Appold & Wenz, under review). Thus, ore fluids in all three districts were relatively Mg enriched and capable of precipitating dolomite, consistent with its abundance as a gangue mineral in all three districts.

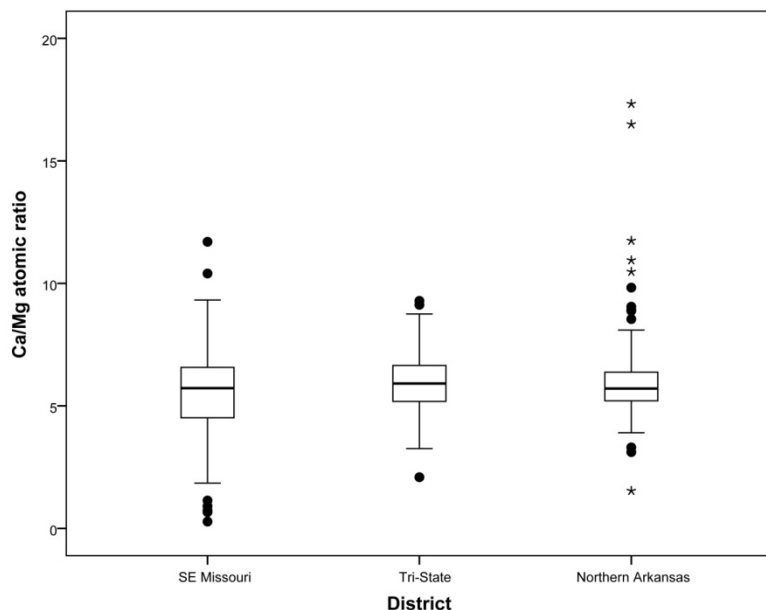


Figure 7. Box plot of atomic Ca/Mg ratios of sphalerite-hosted fluid inclusions from the Southeast Missouri, Tri-State, and Northern Arkansas districts. Here and in succeeding plots, box length represents the interquartile range, i.e. data lying between the 25th and 75th percentile. The horizontal line within each box is the median value. Data ranging within three box lengths of a box edge are plotted as outliers represented as vertical lines extending from the box. Data that are three box lengths beyond a box edge are plotted as filled circles (extreme) or stars (very extreme).

Atomic K/Na ratios in sphalerite-hosted fluid inclusions average about 0.022 in Tri-State and Northern Arkansas and 0.028 in Southeast Missouri (Fig. 8). These values are higher by as much as an order of magnitude than those for sedimentary brines overall, but resemble the elevated K/Na ratios of more saline, deeper, and hotter sedimentary brines (Hanor, 1979; 1994; Sverjensky, 1984). This observation is consistent with hydrologic models of ore formation for the Ozark MVT deposits, in which mineralizing groundwater is shown to have penetrated deeply into the Arkoma basin below its topographic maximum, acquiring heat that it transported northward to the site of ore

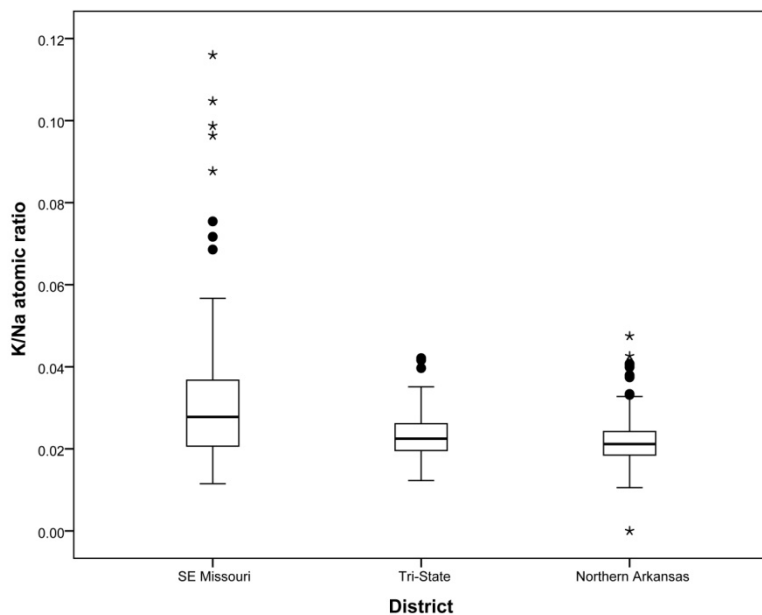


Figure 8. Box plot of atomic K/Na ratios of sphalerite-hosted fluid inclusions from the Southeast Missouri, Tri-State, and Northern Arkansas districts.

(Lentini and Shanks, 1983; Rothbard, 1983; Diehl and Goldhaber, 1995). The Tri-State and Northern Arkansas ores are hosted by younger Ordovician and Mississippian carbonates and are not as close to K rich source rocks.

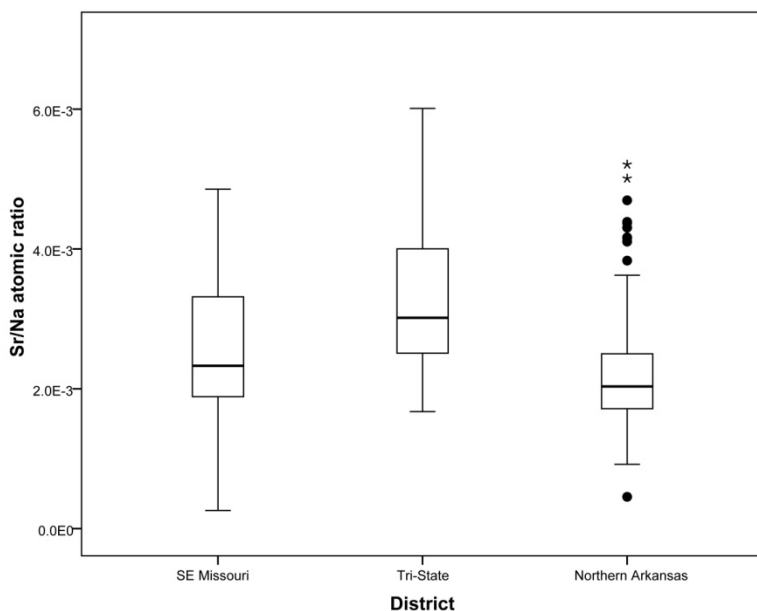


Figure 9. Box plot of atomic Sr/Na ratios of sphalerite-hosted fluid inclusions from the Southeast Missouri, Tri-State, and Northern Arkansas districts.

deposition at shallower burial depths of the foreland (Garven et al., 1993; Appold and Garven, 1999; Appold & Nunn, 2005). In addition to having a higher average value, the range of Southeast Missouri K/Na ratios extends to a higher value of nearly 0.12 whereas the Tri-State and Northern Arkansas ranges reach maximum values of only 0.042 and 0.047, respectively. The high K content of Southeast Missouri ore fluid was likely acquired through interaction with granitic basement rock and the basal arkosic section of the Cambrian Lamotte Sandstone at shallower depths closer to or within the Southeast Missouri district

Atomic Sr/Na ratios in sphalerite-hosted fluid inclusions average about 2.0×10^{-3} in Northern Arkansas, 2.4×10^{-3} in Southeast Missouri, and 3.0×10^{-3} in Tri-State (Fig. 9). These values are typical of sedimentary brines. The reason for these differences is not clear, and the differences are also not very large, but they may reflect differences in the degree of alteration (dolomitization and silicification) of the host limestone, which would have released Sr into solution, and in the original Sr content of the host limestone.

Sphalerite-hosted fluid inclusions from Northern Arkansas have

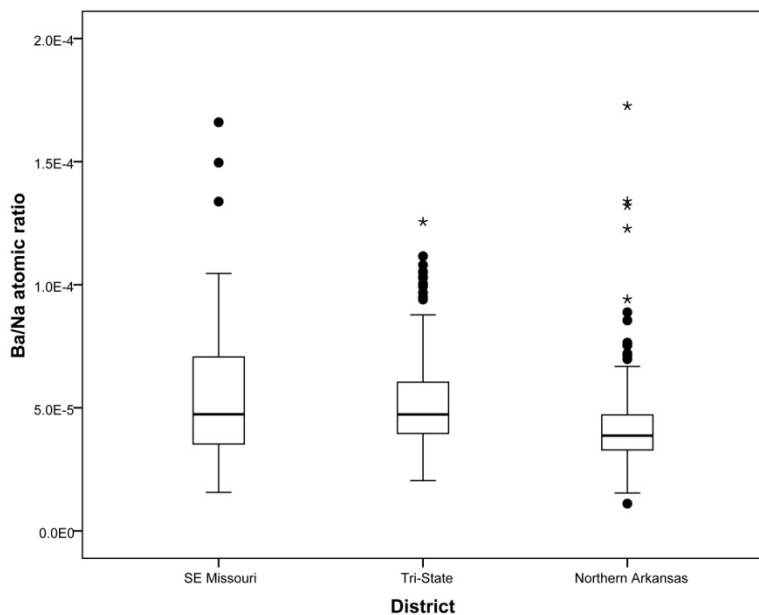


Figure 10. Box plot of atomic Ba/Na ratios of sphalerite-hosted fluid inclusions from the Southeast Missouri, Tri-State, and Northern Arkansas districts.

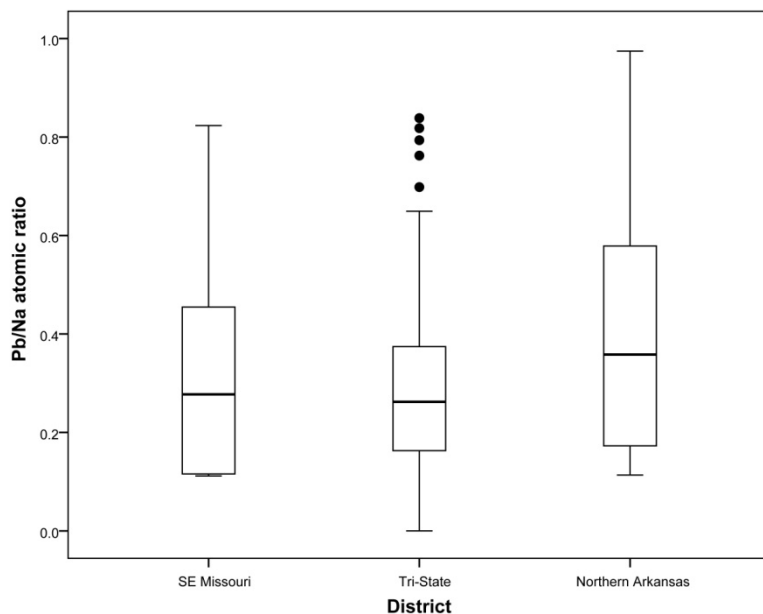


Figure 11. Box plot of atomic Pb/Na ratios of sphalerite-hosted fluid inclusions from the Southeast Missouri, Tri-State, and Northern Arkansas districts.

average atomic Ba/Na ratios of about 4.0×10^{-5} that are slightly lower than the average ratio of 5.0×10^{-5} in Southeast Missouri and Tri-State (Fig. 10). In contrast, atomic Pb/Na ratios in Northern Arkansas are slightly higher at about 4.0×10^{-4} instead of about 2.8×10^{-4} in Southeast Missouri and Tri-State (Fig. 11). The differences among the districts are not very large, though the Northern Arkansas data set has a few very Pb rich outliers at values of around 2100 ppm that suggest the presence of a particularly Pb rich end member fluid in the district.

Summary and Conclusions

The results of this study have confirmed that MVT deposits in the Southeast Missouri, Tri-State, and Northern Arkansas districts precipitated from fluids that resemble typical deep sedimentary basinal brines. The overall compositions of fluid inclusions in the three districts are similar to one another, with TDS concentrations between 208,000 and 235,000 ppm consisting principally of the cations Na, Ca, K, Mg, Sr, and Ba ranked in decreasing order of abundance, with Cl presumed to be the principal anion. Subtle compositional variations existed among ore fluids of the

districts, as evidenced by fluid inclusions hosted by sphalerite. Fluid inclusions from Southeast Missouri are enriched in potassium relative to Tri-State and Northern Arkansas. Northern Arkansas fluid inclusions have the lowest Sr/Na and Ba/Na ratios and the highest Pb/Na ratios

and average TDS concentration of the three districts. The potassium enrichment in Southeast Missouri is most likely related to the ores' proximity to granitic basement rocks. Northern Arkansas and Tri-State ores are located in stratigraphically higher rocks that are not near any potassium rich source rocks. The reasons for the other geochemical differences are currently not clear, but a correlation between Pb concentration and salinity is consistent with the greater solubility of Pb in higher salinity fluids because of the effects of chloride complexing. Why the highest Pb aqueous concentrations should be in the smallest of the three districts could be because the least metal was precipitated from the fluid, perhaps because of a lower supply of sulfide or reductant at the site of ore deposition.

Though Pb concentrations were highest in fluid inclusions from the Northern Arkansas district, each of the districts had a population of Pb rich fluid inclusions with concentrations on the order of at least 100's of ppm in Southeast Missouri and 1000's of ppm in Tri-State and Northern Arkansas. Careful examination of the LA-ICP-MS spectra of these analyses shows that the Pb signals from which the concentrations were computed are in fact consistently associated with the aqueous phase and are unlikely to represent Pb rich mineral inclusions or solid solution. Cu was a more difficult element to quantify and was not successfully detected in Southeast Missouri fluid inclusions. However, some sphalerite-hosted fluid inclusions from Tri-State and Northern Arkansas had Cu concentrations on the order of 1000's of ppm. The Pb and Cu rich fluid inclusions appear to be limited to sphalerite and were not found in any of the gangue mineral hosts. These observations lead to the conclusion that ore deposition in each of the three MVT districts involved invasion of a metal rich brine. The low sulfide concentration that could be carried with these high metal concentrations makes it unlikely that metals and sulfide were transported together in the same solution. Instead, metals were most likely transported either with sulfate in an oxidizing fluid where sulfide mineral deposition was induced by mixing with some kind of a reductant, or in a sulfur poor fluid where sulfide mineral deposition was induced by mixing with a H₂S rich fluid.

To distinguish between these two possibilities, fluid inclusions were analyzed by Raman spectroscopy to try to identify any sulfur species present. Sulfate was not detected in any fluid inclusions analyzed, though its detection limit was relatively high at around 5×10^{-3} molal. H₂S was detected in many sphalerite-hosted fluid inclusions but not in any gangue mineral-hosted fluid inclusions. Though the concentration of H₂S could not be quantified, its prevalence suggests reducing conditions during the time of sulfide mineral precipitation. This conclusion is supported by the coexistence of abundant methane in sphalerite-hosted fluid inclusions from Southeast Missouri, from which a likely log f_{O_2} value between -54 and -55 could be calculated. That H₂S was present and conditions were reducing during the time of sphalerite precipitation does not indicate whether a metal rich fluid mixed with a H₂S rich fluid or whether sulfate in a metal rich fluid was reduced to sulfide by methane or another reductant at the site of ore deposition, as both processes would have resulted in reducing, H₂S rich conditions. However, the fact that methane was present throughout the paragenesis but H₂S only during the time of sphalerite deposition suggests that conditions were generally reducing in the ore districts and sulfur was introduced with metals during times of sphalerite precipitation. This would favor a sulfate reduction model for ore deposition.

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Manuscripts under Review:

Appold, M. S., Wenz, Z. J. (submitted August 4, 2009) Composition of ore fluid inclusions from the Viburnum Trend, Southeast Missouri district, USA: implications for transport and precipitation mechanisms: Economic Geology.

Manuscripts in Preparation:

Wenz, Z. J., Appold, M. S. (in preparation) Regional synthesis of the geochemistry of Mississippi Valley-type ore-forming fluids in the Ozark Plateau: American Journal of Science.

Doctoral Dissertation in Preparation:

Wenz, Z. J. (in preparation) Fluid geochemistry and origin of Mississippi Valley-type mineralization in the Ozark Plateau: University of Missouri—Columbia.

Appendix I

Sample Locations

Sample ID	Latitude (°N)	Longitude (°W)	Location Description
<i>Northern Arkansas district</i>			
NACP	36.34052	92.80845	Copper Head mine
NAEX	36.04055	92.82385	Excelsior mine
NAJP	36.30061	92.90611	Jackpot mine
NALB	36.33995	92.65308	Lost Belle mine
NALD	36.06567	92.74422	Lucky Dog mine
NAMC	36.13052	92.55152	Monte Cristo mine
NAPA	36.13290	92.54938	Philadelphia mine
<i>Southeast Missouri district</i>			
35 8V22	37.65972	91.12667	Casteel mine
81V22	37.65972	91.12667	Casteel mine
MAG13	37.63944	91.12250	Magmont mine
MAG13A	37.63944	91.12250	Magmont mine
VTSW2	37.35972	91.14583	Sweetwater mine
VTSW2E	37.35972	91.14583	Sweetwater mine
VTSW2F	37.35972	91.14583	Sweetwater mine
WF	37.49167	91.10833	West Fork mine
WF2B	37.49167	91.10833	West Fork mine
<i>Tri-State Missouri district</i>			
TSBS3	37.03271	94.75474	Baxter Springs, KS
TSBS5	37.24322	94.42198	Baxter Springs, KS
TSCM2	37.01602	94.85260	Commerce, OK
TSDW2	37.11122	94.41595	Duenweg, MO
TSGY2	36.91210	94.24985	Granby, MO
TSNC1	37.25052	94.44488	Neck City, MO
TSPC2	36.96418	94.81046	Picher, OK
TSPC7	36.97038	94.85997	Picher, OK
TSTR1	37.01602	94.85260	Treece, KS
TSWB3	37.01468	94.86025	Treece, KS
TSWC1	37.15292	94.45368	Webb City, MO

Appendix II

LA-ICP-MS Elemental Composition Analyses of Fluid Inclusions from Ozark MVT Deposits

Sample ID	Mineral Host	Fluid inclusion #	Th1	Th2	Tm1	Tm2	Na ppm	Mg ppm	K ppm	Ca ppm	Cu ppm	Sr ppm	Ba ppm	Pb ppm
<i>Northern Arkansas district</i>														
NAMC1-4	dolomite	1	141	142	-22.8	-22.7	92479		3495			1225	17	
NAMC1-4	dolomite	1	137	138	-22.3	-22.4	89548		4298				22	
NAMC1-4	dolomite	3	136	137	-22.3	-22.4	91034		2593			576	14	
NAEX1-7	dolomite	2	126	127	-21	-21.1	87842		3618			602	14	
NAEX1-7	dolomite	3	127	128	-19.7	-19.8	82533		6258			649	25	
NAEX1-7	dolomite	6	126	127	-21	-21.1	86618						13	
NAJP1-1	dolomite	1	132	133	-21.3	-21.4	88832		3570			943	36	
NAJP1-1	dolomite	1	116	117	-20.8	-20.7	86991		3930			1123	22	
NALD1-1	dolomite	1	132	133	-11.8	-11.9	60388		2017			791	6	1
NALD1-1	dolomite	1	118	119	-11.7	-11.8	59468		3129			787	16	
NALD1-1	dolomite	1	136	137	-18.5	-18.6	81109		3885			1356	9	
NAPA1-1	dolomite	1	118	119	-18.7	-18.6	81291		3669			633	13	
NAPA1-1	dolomite	2	136	137	-23.1	-23.2	91352		4256				53	
NAPA1-1	dolomite	4	135	136	-23.3	-23.4	95002							
NAPA1-1	dolomite	6	115	116	-22.8	-22.7	92767		2628			776	11	
NAPA1-1	dolomite	7	142	143	-23	-23.1	93164		3231			726	19	
NAPA1-1	dolomite	8	146	147	-23	-23.1	92971		3672			949	14	
NAPA1-1	dolomite	9	137	138	-22.7	-22.8	93035						24	
NAPA1-1	dolomite	10	133	134	-22.7	-22.8	92739						38	
NAPA1-1	dolomite	11	122	123	-17.7	-17.6	78353		3653			764		36
NAMC1-4	dolomite	1	141	142	-22.8	-22.7	92479		3495			1225	17	
NAPA1-13	quartz	5	110		-22	-21.9	72057	956	1550	16306		493	10	
NAPA1-13	quartz	7	105	106	-22	-21.9	70497	963	2902	17003		598	29	
NACP1-8	sphalerite	1	109	110	-20.4	-20.3	66457	1577	2184	16570		578	17	
NACP1-8	sphalerite	1	102	103	-22.5	-22.4	62498	1876	1927	24951		546	17	
NACP1-8	sphalerite	2	98	99	-22.7	-22.6	72216	1670	2027	16698		533	16	
NACP1-8	sphalerite	1	108	109	-23.2	-23.1	69090	1828	2650	20003		648	17	
NACP1-8	sphalerite	2	100	101	-23.3	-23.4	66517	2444	3328	21099		724	26	
NAPA1-13B	sphalerite	2	90	91	-21.6	-21.5	66189	1683	3732	18633		397	10	
NAPA1-13B	sphalerite	3	80	81	-21.9	-21.8	71156	1459	2623	15800		481	10	
NALD1-2	sphalerite	1	113	114	-20.1	-20	66839	1732	5398	13012		270	8	
NALD1-2	sphalerite	1	105	106	-19.5	-19.4	64523	1769	2905	15561		334	12	34
NAPA1-13	sphalerite	1	101	102	-21	-21.1	66467	2083	2699	17348		382	19	
NAPA1-13	sphalerite	2	100	101	-21.5	-21.4	66630	1861	2732	18423		405	13	
NAPA1-13	sphalerite	3	139	140	-21	-20.9	59817	2550	1899	22993		554	17	
NACP1-8	sphalerite	1	115	116	-22	-22.1	59050	2199		26508		1127	14	
NAJP1-3	sphalerite	1	99	100	-22.5	-22.4	67898	2606	2430	18110	230	524	19	643
NAJP1-3	sphalerite	2	100	101	-22.5	-22.4	70959	1900	2484	16648	75	535	15	17
NAJP1-3o	sphalerite	1	100	101	-23	-22.9	66006	2510	4203	20373		606	13	
NAMC1-1	sphalerite	1	136	137	-23	-22.9	69483	1810		20091		574	24	
NAMC1-1	sphalerite	2	138	139	-23	-22.9	70368	1806	1541	19251		554	27	

Sample ID	Mineral Host	Fluid inclusion #	Th1	Th2	Tm1	Tm2	Na ppm	Mg ppm	K ppm	Ca ppm	Cu ppm	Sr ppm	Ba ppm	Pb ppm
NAMC1-1	sphalerite	3	133	134	-23	-22.9	68716	2433	1430	19876		674	31	
NAMC1-1	sphalerite	1	110	111	-23.1	-23.2	70829	1856	2411	18589		558	17	
NAMC1-1	sphalerite	2	110	111	-23.1	-23.2	74006	583	3336	16646		393	18	
NAEX1-7	sphalerite	2	129	130	-21	-21.1	52900	1494	3667	21875		882	55	
NAEX1-7	sphalerite	1	115	116	-16	-16.1	51517	1434	2644	14151		845	11	103
NAEX1-7	sphalerite	2	113	114	-16	-16.1	53236	1706	2193	17001		1057	9	
NAEX1-7	sphalerite	3	113	114	-16	-16.1	53561	1202	3635	15534		959	24	1949
NAEX1-7	sphalerite	4	113	114	-16	-16.1	52719	2067	2004	16833		825	11	853
NAEX1-7	sphalerite	1	113	114	-20.3	-20.4	66860	1608	2068	16317		535	15	83
NAEX1-7	sphalerite	2	113	114	-20.5	-20.6	66443	1700	1477	17527		434	10	
NACP1-8	sphalerite	2	96	97	-22.1	-22.2	67583	2116	2155	19053		649	19	
NACP1-8	sphalerite	2	86	87	-21.5	-21.6	66222	1481	2385	19654		638	17	
NAEX1-14	sphalerite	1	109	110	-21.9	-22	66775	2374	4589	17380		516	16	
NAEX1-14	sphalerite	2	110	111	-22.2	-22.1	72091	1638	2244	15632		496	15	
NAEX1-2	sphalerite	1	101	102	-22.9	-22.8	70647	1841	2394	18129		561	18	
NAEX1-2	sphalerite	2	100	101	-22.9	-22.8	72204	1644	1905	17281		610	22	
NAEX1-2	sphalerite	3	100	101	-22.9	-22.8	72039			18187		613	21	
NAJP1-10	sphalerite	1	103	104	-22.7	-22.8	69036	2053	1961	18065	696	562	19	47
NAJP1-10	sphalerite	2	101	102	-22.6	-22.7	68467	2584	2320	18635	1948	621	20	283
NAJP1-10	sphalerite	3	102	103	-22.6	-22.7	66272	2120	2052	18407	2846	705	20	
NAJP1-10	sphalerite	4	102	103	-22.7	-22.8	68756	2018	1992	18595	435	479	14	95
NALB1-1	sphalerite	1	88	89	-22.8	-22.9	68570	2169	2155	19658		653	16	29
NALB1-1	sphalerite	2	88	89	-22.8	-22.9	68380	2456		16796	1671	510	12	3211
NALB1-1	sphalerite	1	107	106	-21.9	-22	69839	1900	2035	16974		549	17	
NALB1-1	sphalerite	2	107	108	-22	-22.1	69147	2262	2193	17206		567	21	
NALD1-4	sphalerite	4	115	116	-22.7	-22.8	67564	1467	3023	20668		775	53	
NAMC1-1	sphalerite	1	99	100	-22.2	-22.3	69720	1950	2478	17395		559	18	
NAMC1-1	sphalerite	2	102	103	-22.2	-22.3	70919	1515	2503	16854		615	18	
NAMC1-1	sphalerite	3	102	103	-22.2	-22.3	68275	1972	1863	19141		514	23	
NAMC1-1	sphalerite	4	102	103	-22.2	-22.3	70015	1977	2526	17039		579	19	
NAMC1-1	sphalerite	5	103	104	-22.2	-22.3	70184	1416	2660	17609		544	16	
NAMC1-1	sphalerite	6	103	104	-22.2	-22.3	70677	1753	1687	17355		532	20	
NAMC1-1	sphalerite	1	106	107	-22.1	-22.2	70806	1694	2183	16765		511	16	
NAMC1-1	sphalerite	2	99	100	-22.1	-22.2	71436	1797	2201	16004		547	14	
NAMC1-1	sphalerite	1	129	130	-22.2	-22.3	71253	1706	2696	15298	1128	473	16	164
NAMC1-1	sphalerite	2	133	134	-22.2	-22.3	74764	1726		14824		502	18	
NAMC1-1	sphalerite	4	129	130	-22.2	-22.3	71250	1494	2481	16668		506	17	
NAMC1-1	sphalerite	2	124	125	-22.2	-22.3	72587	1741	1740	15614		485	17	
NAMC1-1	sphalerite	3	128	129	-22.2	-22.3	70868	1345	3342	16627		522	15	
NAMC1-1	sphalerite	4	128	129	-22.2	-22.3	72254	1974		16131		505	10	
NAMC1-1	sphalerite	2	105	106	-22.3	-22.4	69188	2076	2240	18129		519	12	
NAMC1-1	sphalerite	3	105	106	-22.3	-22.4	73186	1200	2365	15639	3198	471	18	236
NAMC1-1	sphalerite	4	105	106	-22.3	-22.4	72216	1706	2065	15984	675	529	15	82
NAMC1-1	sphalerite	5	105	106	-22.3	-22.4	71960	1733	1448	16630		491	15	
NAMC1-1	sphalerite	6	105	106	-22.3	-22.4	69822	2083	2307	17475		540	16	
NAMC1-1	sphalerite	8	105	106	-22.3	-22.4	69822	2083	2307	17475		540	16	
NAPA1-13	sphalerite	1	101	102	-21.1	-21.2	69480	1622	2665	15513		357	14	

Sample ID	Mineral Host	Fluid inclusion #	Th1	Th2	Tm1	Tm2	Na ppm	Mg ppm	K ppm	Ca ppm	Cu ppm	Sr ppm	Ba ppm	Pb ppm
NAPA1-13	sphalerite	2	101	102	-21.1	-21.2	62493	2530	3482	19884		646	26	
NAPA1-13	sphalerite	5	101	102	-21.1	-21.2	69969	1490	2632	15275		357	11	
NAPA1-13	sphalerite	6	101	102	-21.1	-21.2	67913	1798	2381	16861		416	13	
NAPA1-13	sphalerite	7	102	103	-21.1	-21.2	69659	1614	2852	15224		368	14	
NAPA1-13	sphalerite	8	101	102	-21.1	-21.2								
NAMC1-1	sphalerite	1	103	104	-22.3	-22.4	73212	1744	2387	14839		456	19	
NAMC1-1	sphalerite	3	103	104	-22.3	-22.4	74659	1335	1439	14748		447	19	
NAMC1-1	sphalerite	4	103	104	-22.3	-22.4	70888	2038	2399	16523		497	17	
NAMC1-1	sphalerite	6	107	108	-22.3	-22.4	71190	1505	1717	17444		539	14	
NAMC1-1	sphalerite	7	108	109	-22.3	-22.4	71988	1703	2392	15990		503	14	
NAMC1-1	sphalerite	8	107	108	-22.3	-22.4	72871	1728	2010	15384		530	24	
NAPA1-13	sphalerite	1	94	95	-21	-20.9	70239	1537	2604	14490	334	379	13	52
NAPA1-13	sphalerite	2	100	101	-21	-21.1	69183	1957	2923	14259	743	407	17	75
NAPA1-13	sphalerite	1	97	98	-21.3	-21.4	70749	1691	2765	14653		359	14	
NAPA1-13	sphalerite	2	101	102	-21.3	-21.4	69991	1736	2714	15340	158	328	14	137
NAPA1-13	sphalerite	1	104	105	-21.4	-21.5	54930	2674	3545	27287		658	17	
NAPA1-13	sphalerite	3	103	104	-21.5	-21.6	70897	1666	2751	15017		383	13	
NAPA1-13	sphalerite	4	103	104	-21.5	-21.6	69871	1217	3225	16235		439	6	
NALD1-2	sphalerite	1	124	125	-20.9	-21	70857	1696	3341	13230		318	13	
NALD1-2	sphalerite	2	116	117	-20.9	-21	67370	1894	3336	16149		329	12	
NALD1-2	sphalerite	1	101	102	-21.5	-21.4	74477	1301	2708	12054		366	12	
NALD1-2	sphalerite	2	101	102	-21.5	-21.4	74561	1586	2828	11485		368	21	
NALD1-4	sphalerite	1	105	106	-19.8	-19.9	61659	2244	2451	18578		733	12	
NALD1-4	sphalerite	2	120		-22.3	-22.4	73697	1365	2482	14839		503	12	
NALD1-4	sphalerite	1	121	122	-20.3	-20.4	62841	1953	2595	18820		998	21	60
NALD1-4	sphalerite	2	144	145	-22.3	-22.4	61402	1405	3162	25354		821	33	56
NALD1-4	sphalerite	3	144	145	-22.3	-22.4	54302	1210	2178	32891		688	43	89
NALD1-4	sphalerite	4	144	145	-22.3	-22.4	69260	1241	2991	18512		773	35	73
NALD1-4	sphalerite	5	144	145	-22.3	-22.4	57575	1766	2795	28610		795	32	90
NALD1-4	sphalerite	6	144	145	-22.3	-22.4	67678	1518	3010	19547		801	50	45
NAPA1-13	sphalerite	1	100	101	-21.3	-21.2	68746	1725	2788	15914	69	503	10	275
NAPA1-13	sphalerite	2	100	101	-21.4	-21.3	68779	1708	2722	16390		399	16	104
NAPA1-13	sphalerite	3	100	101	-21.4	-21.3	71173	1522	2770	14381		408	10	183
NAPA1-13	sphalerite	1	98	99	-21.5	-21.4	70043	1839	2666	15378		387	12	242
NAPA1-13	sphalerite	3	98	99	-21.5	-21.4	69547	1599	2866	16041		377	14	
NAPA1-13	sphalerite	4	98	99	-21.5	-21.4	68364	1764	2517	17130		381	16	
NAPA1-1	sphalerite	1	105	106	-20.9	-20.8	68251	1768	2746	15614		438	13	
NAPA1-1	sphalerite	2	105	106	-20.9	-20.8	62250	1923	3534	20203		677	14	
NAPA1-1	sphalerite	3	105	106	-20.9	-20.8	68117	1649	2694	15960		409	14	
NAPA1-1	sphalerite	4	105	106	-20.9	-20.8	68433	1818	2774	15357		436	15	
NACP1-8	sphalerite	1	111	112	-22.4	-22.5	70336	1843	2225	17068	591	612	16	128
NACP1-8	sphalerite	2	111	112	-22.4	-22.5	69274	1794	2201	18043	719	641	18	59
NACP1-8	sphalerite	3	111	112	-22.4	-22.5	66033	1954	2442	20077	1265	796	19	124
NACP1-8	sphalerite	1	108	109	-22.6	-22.5	68732	1980	2358	18974		650	15	
NACP1-8	sphalerite	2	102	103	-22.6	-22.5	71203	1697	2274	17210		578	15	
NACP1-8	sphalerite	3	102	103	-22.6	-22.5	74456	2124	2231	13678		532	17	
NACP1-8	sphalerite	4	102	103	-22.6	-22.5	68668	1692	2510	19330		657	15	

Sample ID	Mineral Host	Fluid inclusion #	Th1	Th2	Tm1	Tm2	Na ppm	Mg ppm	K ppm	Ca ppm	Cu ppm	Sr ppm	Ba ppm	Pb ppm
NAEX1-2	sphalerite	1	94	95	-22.5	-22.4	64877	2404	2451	21520		797	20	
NAEX1-2	sphalerite	2	94	95	-22.5	-22.4	66561	2108	2392	20529		653	18	
NAEX1-2	sphalerite	3	94	95	-22.5	-22.4	69896	1755	1908	18343		579	28	
NAEX1-2	sphalerite	1	107	108	-22.6	-22.5	72111	1779	2252	16338		482	15	
NAEX1-2	sphalerite	2	100	101	-22.6	-22.5	70282	2200	2528	17225		492	16	306
NAEX1-2	sphalerite	3	112	113	-22.6	-22.5	68516	2255	2025	19051		600	5	257
NAEX1-2	sphalerite	1	104	105	-21.7	-21.8	68671	1830	2616	16907		483	17	855
NAEX1-2	sphalerite	2	104	105	-21.9	-22	71438	2145	1857	15325		486	12	
NAEX1-2	sphalerite	3	105	106	-21.9	-22	64149	2177	2658	21282		694	16	
NAEX1-2	sphalerite	5	103	104	-21.7	-21.8	68736	1532	2648	17376		565	14	
NAEX1-7	sphalerite	1	113	114	-21.7	-21.8	67342	1871	2220	18679		604	17	
NAEX1-7	sphalerite	2	107	108	-21.7	-21.8	62188	2159	2413	22808		695	17	2073
NAJP1-3	sphalerite	1	99	100	-21.4	-21.5	67785	1922	2327	17472		526	20	79
NAJP1-3	sphalerite	2	99	100	-21.4	-21.5	71118	1532	2088	15157		487	15	49
NALD1-4	sphalerite	1	110	109	-22.2	-22.1	69373	1973	2133	17685		529	17	45
NALD1-4	sphalerite	7	116	117	-21.7	-21.8	69096	1809	2042	17327		531	16	60
NALD1-4	sphalerite	8	110	111	-21.4	-21.5	67154	1842	2196	18016		896	14	50
NALD1-4	sphalerite	9	112	113	-21.4	-21.5	67353	1955	2464	17490		896	14	<46
NALD1-4	sphalerite	10	112	113	-21.4	-21.5	64045	2263	2849	19747		1014	16	152
<i>Southeast Missouri district</i>														
MAG13A	dolomite	1	157	158	-22.6	-22.5	91910		3598				34	
MAG13A	dolomite	1	154	155	-22.6	-22.5	91365		3429				38	18
MAG13A	dolomite	1	119	120	-22.4	-22.5	91338		3840				45	4
VTW2F	dolomite	1	106	107	-17.5	-17.6	79154		2747				9	14
VTW2F	dolomite	1	128	129	-22.1	-22	90217		4076			603	26	6
VTW2F	dolomite	1	130	131	-6.6	-6.7	38252		1885				6	3
VTW2F	dolomite	2	124	125	-22.3	-22.4	91580		3113			510	44	
VTW2F	dolomite	1	105	106	-19.8	-19.9	85345		2977			702	22	14
WF2B	dolomite	1	136	137	-22.6	-22.5	91285		4359				57	
81V22	dolomite	4	126	127	-21.7		90271		2857				13	
VTW2	dolomite	1	125	126	-5.5	-5.4	32085		2032				7	
VTW2	dolomite	3	110	111	-22.4	-22.5	91869		2542			829	30	22
VTW2	dolomite	4	125	126	-22.4	-22.5	91241		4109			1064	54	
VTW2	dolomite	6	118	119	-22.4	-22.5	91725		3235			633	23	
VTW2	dolomite	7	121	122	-22.4	-22.5	92135		3017			815	30	
VTW2	dolomite	9	121	122	-22.4	-22.5	91981		2725			295	25	16
VTW2	dolomite	1	116	117	-22.7	-22.8	93011		2817			869	29	
VTW2	dolomite	2	116	117	-22.7	-22.8	92050		3993				42	
VTW2	dolomite	3	119	120	-22.7	-22.8	92409		3399			149	21	31
VTW2	dolomite	6	123	124	-22.2	-22.3	91896		2013			681	24	31
35_8V22	sphalerite	1	71	72	-2.5		12265	1455	750	670		47		
35_8V22	sphalerite	1	89	90	-23	-23.1	74290	5097	7106	7614		233		
35_8V22	sphalerite	1	75	76	-20.8	-20.7	74671	1175	1462	11075		270	9	
35_8V22	sphalerite	2	101	102	-22.8	-22.7	73201	1878	4507	14068		542	7	
35_8V22	sphalerite	3	102	103	-22.8	-22.7	70976		2266	18151		496	17	
WF2	sphalerite	1	111	112	-20.4	-20.5	74917	1220	2135	9791		346	10	

Sample ID	Mineral Host	Fluid inclusion #	Th1	Th2	Tm1	Tm2	Na ppm	Mg ppm	K ppm	Ca ppm	Cu ppm	Sr ppm	Ba ppm	Pb ppm
WF2	sphalerite	1	107	108	-20.3	-20.4	68944	1492	2358	14429		441	15	
MAG13	sphalerite	3	109	110	-15.5	-15.4	54347	1508	2014	14516		811	14	
MAG13	sphalerite	1	115	116	-21.6	-21.7	69255	1494	2433	16913		844	29	
MAG13	sphalerite	1	105	106	-15.5	-15.4	59199	1027	2004	11202		570	12	
MAG13	sphalerite	2	109	110	-15.5	-15.4	53836			14946		908		
MAG13	sphalerite	3	109	110	-15.5	-15.4	54365	1797	2316	14161		829	21	
MAG13	sphalerite	1	117	118	-23	-23.1	75203	782	3552	15080		595	20	
MAG13	sphalerite	3	118	119	-23.2	-22.2	77395		3883	12879		619	29	
MAG13A	sphalerite	1	115	116	-15.7	-15.8	60113	1054	2267	10915		718	19	165
MAG13A	sphalerite	2	107	108	-15.6	-15.5	52809	1640	2720	15731		977	18	256
MAG13A	sphalerite	3	112	113	-15.3	-15.2	54056	1364	2562	14236		930	16	52
MAG13A	sphalerite	4	104	105	-15.3	-15.2	52740	1580	2008	15588		830	12	129
MAG13A	sphalerite	5	115	116	-15.3	-15.2	52107	1483	2660	15795		921	15	52
MAG13A	sphalerite	1	110	111	-15.3	-15.2	54738	1014	2612	14133		836	13	56
MAG13A	sphalerite	4	113	114	-15.3	-15.2	55667	839	1371	14385		822	27	
VTW2E	sphalerite	4	99	100	-20.7	-20.8	63060	2166	6080	16857		1051	56	
VTW2E	sphalerite	1	99	100	-20.7	-20.8	59528	4593	9996	14462		339	6	
WF2B	sphalerite	1	105	106	-22.5	-22.4	69344	1955	2053	18484		564	15	
WF2B	sphalerite	2	106	107	-22.5	-22.4	68433	1958	2271	19024		777	18	
Tri-State district														
TSGY2-1	calcite	2	67	68	-4.2		26136						13	
TSGY2-1	calcite	3	66	67	-4.2		25650		986				9	
TSGY2-1	calcite	2	77	78	-4.2		25930		685				32	
TSNC1-2	dolomite	1	108	109	-18.5	-18.6	81126		3801			894	21	
TSNC1-2	dolomite	2	128	129	-18.5	-18.6	82461		2211			301	8	
TSNC1-2	dolomite	3	128	129	-18.5	-18.6	81377		3124				17	
TSNC1-2	dolomite	4	108	109	-18.5	-18.6	81617		3236			1021	15	
TSNC1-2	dolomite	1	120		-22	-22.1	89205		5326				35	
TSNC1-2	dolomite	2	120	121	-22	-22.1	91067		2896				49	
TSNC1-2	dolomite	4	121	122	-22	-22.1	90559		3642			1369	37	
TSPC7-1	dolomite	1	131	132	-22.9	-22.8	92472		3904				64	
TSPC7-1	dolomite	1	129	130	-22.9	-22.8	90950		5857			1205	22	
TSPC7-1	dolomite	1	122	123	-22.9	-22.8	92174		4192			1310	62	
TSDW2-2	quartz	1	105	106	-21.8	-21.9	77861	974		11246		520	15	
TSDW2-2	quartz	3	106	107	-22	-22.1	71982	1702	1498	15804		527	23	
TSDW2-2	quartz	1	62	63	-21.4	-21.5	76179	1011	1746	11452		383	15	
TSDW2-2	quartz	4	67	68	-21.7	-21.8	66752	1050		19868		633	18	
TSDW2-2	quartz	1	100	101	-22	-22.1	79902	553	1336	9786		344	8	
TSDW2-2	quartz	1	100	101	-22.2	-22.3	73998	144	2403	15960		516	16	
TSDW2-2	quartz	2	91	92	-22.1	-22.2	81135		2178	9003		291	7	9
TSWC1-2	quartz	5	114	115	-22.7	-22.6	72486	1833	2218	16056		515	16	
TSWC1-2	quartz	6	78		-22.7	-22.6	70966	1687	2501	17487		585	16	1
TSWC1-2	quartz	1	133	134	-22.5	-22.6	74041	441	2052	16525		471	13	1
TSWC1-2	quartz	2	109	110	-22.6	-22.7	80244	962	2527	10046		341	13	2
TSWC1-2	quartz	5	112	113	-22.6	-22.7	79650	714	1788	11214		371	14	
TSWC1-2	quartz	1	140+		-22.1	-22	78634	705	2466	10639		323	15	3

Sample ID	Mineral Host	Fluid inclusion #	Th1	Th2	Tm1	Tm2	Na ppm	Mg ppm	K ppm	Ca ppm	Cu ppm	Sr ppm	Ba ppm	Pb ppm
TSWC1-2	quartz	2	86	87	-22.1	-22	76550	51	1794	13859		441	17	2
TSWC1-2	quartz	3	122	123	-22.4	-22.5	75741	303	2371	14806		430	17	
TSWC1-2	quartz	4	139	140	-22.4	-22.5	76776	264	2267	13988		417	17	
TSBS3-2	sphalerite	2	98	99	-15.8	-15.7	52667	1764	2339	16562		923	18	
TSBS3-2	sphalerite	3	108	109	-15.8	-15.7	50816	1839	2943	17772		878	12	
TSBS3-2	sphalerite	5	113	114	-15.8	-15.7	53875	1271	1804	16582		831	15	
TSBS3-2	sphalerite	6	101	102	-15.8	-15.7	49565	1761	3509	18686		812	10	
TSBS3-2	sphalerite	7	94	95	-15.9	-15.8	58859	1455		12305		1018	11	
TSBS3-2	sphalerite	10	97	98	-15.8	-15.7	50822	1765	2309	18566		916	22	
TSBS3-2	sphalerite	1	105	106	-20.8	-20.9	73195	1026	1527	12668		881	23	
TSBS3-2	sphalerite	2	100	101	-21.1	-21	60946	1716		22971		884	16	
TSNC1-1	sphalerite	4	99	100	-22.6	-22.7	80663	3856				628		785
TSNC1-1	sphalerite	5	110	111	-22.6	-22.7	66637	1835	4498	18719		837	27	670
TSNC1-1	sphalerite	6	94	95	-22.6	-22.7	62986	5497		18940		446	26	155
TSDW2-8	sphalerite	1	101	102	-22.6	-22.7	65993	3024		20934		715	15	34
TSDW2-8	sphalerite	2	101	102	-22.6	-22.7	65708	1916	2082	22320		484	10	50
TSDW2-8	sphalerite	1	99	100	-22.9	-23	70672	2256	2581	17564		570	20	22
TSDW2-8	sphalerite	2	99	100	-23	-23.1	70593	2283	2664	17767		573	20	19
TSDW2-8	sphalerite	1	93	94	-22.9	-23	66186	2867	2725	20598		792	9	18
TSDW2-8	sphalerite	1	91	92	-22.6	-22.7	66889	2247	3025	20090		536	16	
TSDW2-8	sphalerite	1	97	98	-22.6	-22.7	72095	1985	2313	16224		499	16	13
TSBS5-2	sphalerite	1	118	119	-22.1	-22.2	66299	1577	3187	19773		770	39	868
TSBS5-2	sphalerite	3	116	117	-22.1	-22.2	67064	1603	2849	19462		768	29	480
TSBS5-2	sphalerite	4	118	119	-22.1	-22.2	70243			18535		811	47	1165
TSCM2-1	sphalerite	2	112	113	-16.8	-16.9	57636	2073	2124	14759		1009	15	435
TSCM2-1	sphalerite	3	112	113	-17.1	-17.2	59599	1579	2634	14250		823	11	
TSCM2-1	sphalerite	4	112	113	-16.8	-16.9	56519	1646	1865	16662		862	17	
TSCM2-1	sphalerite	1	114	115	-18.1	-18.2	60238	1580	2230	16579		867	10	
TSCM2-1	sphalerite	2	115	116	-18.3	-18.4	60339	1917		16440		919	22	
TSCM2-1	sphalerite	3	114	115	-18.1	-18.2	62315	1457	2136	14902		878	12	
TSDW2-8	sphalerite	1	106	107	-23.3	-23.4	75745	1907	2129	14684		489	15	77
TSDW2-8	sphalerite	2	105	106	-23.3	-23.4	75436	1752	2315	15089		481	18	21
TSDW2-8	sphalerite	3	105	106	-23.3	-23.4	72634	1961	2165	17386		588	19	50
TSDW2-9	sphalerite	1	107	108	-23.1	-23.2	67970	1479	2541	20345	1586	671	19	104
TSDW2-9	sphalerite	2	108	109	-23.1	-23.2	71773	1760	1731	16931	1655	715	19	105
TSDW2-9	sphalerite	3	103	104	-23.1	-23.2	72193	2002	2113	16114	1486	605	16	167
TSDW2-9	sphalerite	4	103	104	-23.1	-23.2	68693	2193	2306	18975	1449	595	18	130
TSDW2-9	sphalerite	5	103	104	-23.1	-23.2	67682	2119	2719	20903	1166	584	15	956
TSGY2-3	sphalerite	1	108	109	-22.9	-23	64576	1903	2870	23235		982	28	
TSGY2-3	sphalerite	2	108	109	-23.1	-23	69321	1713	2165	19977		804	27	
TSGY2-3	sphalerite	3	107	108	-23.2	-23.1	66980	1436	3126	21984		952	32	
TSPC2-1	sphalerite	1	118	119	-23	-23.1	71869	1965	1878	17604		622	14	259
TSPC2-1	sphalerite	2	118	119	-23.1	-23.2	68792	1874		20848		634	17	279
TSPC2-1	sphalerite	4	122	123	-23	-23.1	69778	1981	2032	19389		624	23	233
TSPC2-1	sphalerite	5	121	122	-23.1	-23.2	70074	2533		18846		723	19	
TSPC2-1	sphalerite	6	120	121	-23	-23.1	66349	2108	4752	20481		635	16	637
TSPC2-1	sphalerite	1	106	107	-22.7	-22.8	72891	2561		15401		605	9	

Sample ID	Mineral Host	Fluid inclusion #	Th1	Th2	Tm1	Tm2	Na ppm	Mg ppm	K ppm	Ca ppm	Cu ppm	Sr ppm	Ba ppm	Pb ppm
TSPC2-1	sphalerite	6	105	106	-22.7	-22.8	71640	1703	2639	16975		628	14	
TSOR2-3	sphalerite	1	109	110	-23.1	-23.2	71694	2210	2115	17479		620	23	
TSPC2-1	sphalerite	1	108	109	-22.7	-22.8	69861			21221		786	19	
TSPC2-1	sphalerite	2	108	109	-22.7	-22.8	68879	1610	2505	19597		812	41	
TSPC2-1	sphalerite	3	108	109	-22.7	-22.8	68057	1316	3894	19794		839	43	423
TSPC2-1	sphalerite	1	122	123	-22.6	-22.7	71917	1250	3601	16418		692	33	
TSPC2-1	sphalerite	2	112	113	-22.6	-22.7	65006	1563	2992	22552		973	41	69
TSPC2-1	sphalerite	1	112	113	-22.8	-22.9	72299	1590	2301	17009		599	15	
TSPC2-1	sphalerite	2	111	112	-22.8	-22.9	70626	1823	2328	18165		645	16	
TSPC2-1	sphalerite	3	111	112	-22.8	-22.9	63950	2348	2584	23294		770	17	
TSTR1-7	sphalerite	1	107	108	-21.2	-21.3	70485	1533	2352	14925		721	21	4
TSTR1-7	sphalerite	2	111	112	-21.2	-21.3	64972	2097	2933	18603		1009	20	7
TSTR1-7	sphalerite	4	109	110	-21.2	-21.3	70529	1329	2197	15279		675	18	73
TSTR1-7	sphalerite	5	112	113	-21.2	-21.3	68691	1939	2693	15690		751	24	113
TSTR1-7	sphalerite	6	107	108	-21.2	-21.3	69952	1549	2645	15202		684	21	32
TSTR1-7	sphalerite	7	109	110	-21.2	-21.3	67927	1812	2467	16807		707	18	12
TSTR1-7	sphalerite	8	109	110	-21.2	-21.3	65895	1970	2946	17796		848	30	476
TSTR1-7	sphalerite	9	110	111	-21.2	-21.3	63897	2899	2452	18924		798	20	109
TSTR1-7	sphalerite	10	111	112	-20.6	-20.7	64852	1833	2630	17937		901	19	
TSTR1-7	sphalerite	11	107	108	-21.2	-21.3	63624	2507	3032	19226		960	16	
TSWB3-9	sphalerite	1	115	116	-23.1	-23.2	73872	1586	2448	16182		551	16	
TSWB3-9	sphalerite	2	117	118	-23.1	-23.2	71405	1737	1941	18519		647	15	173
TSWB3-9	sphalerite	6	119	120	-23.1	-23.2	73733	1413	1663	16990		713	15	
TSWB3-9	sphalerite	8	118	119	-23.1	-23.2	73393	1540	2252	16796		584	22	
TSWB3-9	sphalerite	9	123	124	-23.1	-23.2	72760	1595	2888	16821		655	12	
TSWB3-9	sphalerite	12	119	120	-23.1	-23.2	73924	1399	2660	16194		637	21	249
TSBS5-2	sphalerite	1	109	110	-22.4	-22.5	71937	1651	2477	16230		580	16	116
TSBS5-2	sphalerite	1	120	121	-12.3	-12.4	44203	1629	1793	14391		722	13	
TSBS5-2	sphalerite	3	119	120	-12.3	-12.4	47925	1020	1733	11935		633	14	
TSBS5-2	sphalerite	1	130	131	-22.9	-22.8	69120	1711	2965	19216		705	40	
TSBS5-2	sphalerite	2	130	131	-22.9	-22.8	66401	2105	3808	20548		756	28	
TSBS5-2	sphalerite	3	130	131	-22.9	-22.8	67814	1538	3083	20540		767	36	
TSBS5-2	sphalerite	4	130	131	-22.9	-22.8	66229	1761	3185	21506		916	50	
TSBS5-2	sphalerite	5	130	131	-22.9	-22.8	67042	1508	2872	21410		802	41	
TSBS5-2	sphalerite	1	110	111	-22.4	-22.5	67926	1891	2728	19327		694	16	166
TSBS5-2	sphalerite	2	108	109	-22.4	-22.5	71247	1777	2602	16583		604	17	42
TSBS5-2	sphalerite	3	107	108	-22.4	-22.5	69608	1799	2201	18295		660	19	202
TSBS5-2	sphalerite	4	111	112	-22.4	-22.5	65767	2153	2742	20862		792	18	
TSBS5-2	sphalerite	5	108	109	-22.4	-22.5	68036	2032	2265	19353		678	18	
TSBS5-2	sphalerite	6	110	111	-22.4	-22.5	68775	1756	2359	18986		697	22	
TSCM2-1	sphalerite	1	105	106	-18.3	-18.2	58741	2197	2675	16959		975	17	
TSCM2-1	sphalerite	2	105	106	-18.3	-18.2	59822	2107	2272	16233		1189	15	144
TSCM2-1	sphalerite	3	105	106	-18.1	-18	57865	1842	2545	17838	812	966	17	78
TSCM2-1	sphalerite	4	106	107	-18.3	-18.2	59328	1335	2909	17511		925	18	
TSCM2-1	sphalerite	5	107	108	-18.3	-18.2	58350	1893	2300	17995		991	18	117
TSCM2-1	sphalerite	7	109	110	-18.1	-18	57053	2407	2810	17580		1001	16	
TSCM2-1	sphalerite	2	103	104	-18	-18.1	59155	1849	2347	16801		935	16	15

Sample ID	Mineral Host	Fluid inclusion #	Th1	Th2	Tm1	Tm2	Na ppm	Mg ppm	K ppm	Ca ppm	Cu ppm	Sr ppm	Ba ppm	Pb ppm
TSCM2-1	sphalerite	1	105	106	-18	-17.9	66489	1491	1589	11087		554	10	66
TSCM2-1	sphalerite	2	109	110	-18	-17.9	59941	1760	2446	15880		925	18	
TSCM2-1	sphalerite	3	103	104	-18	-17.9	58621	1880	2738	16709		950	12	53
TSCM2-1	sphalerite	5	109	110	-18	-17.9	61293	1667	2449	14819		849	17	
TSNC1-2	sphalerite	1	96	97	-23.1	-23	69613	2041	2472	19146		638	18	
TSNC1-2	sphalerite	2	98	99	-23.1	-23	66942	1962	2525	21631		704	19	
TSNC1-2	sphalerite	3	98	99	-23.1	-23	71868	1392	2337	18097		622	20	
TSNC1-2	sphalerite	4	101	102	-23.1	-23	69214	1931	2532	19605		673	19	
TSNC1-2	sphalerite	5	97	98	-23.1	-23	68669	1900	2931	19829		738	20	
TSNC1-2	sphalerite	6	96	97	-23.1	-23	70551	1669	2940	18460		682	20	
TSNC1-2	sphalerite	8	101	102	-23.1	-23	68973	1768	2602	20018		660	17	
TSNC1-2	sphalerite	1	94	95	-22.4	-22.5	70606	1638	2279	17555		661	14	
TSWB3-9	sphalerite	1	120	121	-22.9	-22.8	68984	2356	2426	18755		795	15	
TSWB3-9	sphalerite	2	120	121	-22.9	-22.8	67676	2168	2123	20464		739	19	
TSWB3-9	sphalerite	4	121	122	-22.9	-22.8	68793	2089	2218	19500		719	17	
TSWB3-9	sphalerite	5	120	120	-22.9	-22.8	66713	2416	2185	20978		701	21	
TSWB3-9	sphalerite	6	121	122	-22.9	-22.8	67633	2372	2478	19994		703	19	
TSWB3-9	sphalerite	7	120	121	-22.9	-22.8	69757	2008	2410	18647		640	16	
TSTR1-7	sphalerite	2	107	108	-21.4	-21.5	65711	1900	2399	19142		855	21	
TSTR1-7	sphalerite	3	109	110	-21.2	-21.3	65971	1808	2534	18412		805	25	182
TSTR1-7	sphalerite	5	110	111	-21.2	-21.3	65488	1949	2581	18672		866	24	
TSTR1-7	sphalerite	6	111	112	-20.7	-20.8	60241	1910	2756	22184		947	20	21
TSTR1-7	sphalerite	7	110	111	-20.7	-20.8	62942	1885	2584	19867		930	21	
TSTR1-7	sphalerite	8	107	108	-20.7	-20.8	61334	1847	2697	21278		998	18	
TSTR1-7	sphalerite	9	110	111	-20.7	-20.8	65523	2009	2407	17524		812	20	276
TSTR1-7	sphalerite	10	110	111	-20.7	-20.8	62395	2038	2386	20309		896	27	110
TSTR1-7	sphalerite	11	111	112	-22.4	-22.5	58873	2590	2814	26325		1082	35	10
TSTR1-7	sphalerite	12	110	111	-22.4	-22.5	66298	2744	2802	19364		985	32	62
TSTR1-7	sphalerite	13	111	112	-22.4	-22.5	66527	2432	2453	19837		993	21	165
TSTR1-7	sphalerite	14	111	112	-21.8	-21.9	66273	1797	2533	19708		707	27	63
TSTR1-7	sphalerite	15	108	109	-22.9	-22.8	59962	2179	2544	26975		1139	27	15
TSTR1-7	sphalerite	17	112	113	-22.9	-22.8	68953	1593	2723	19676		757	28	87
TSWC1-3	sphalerite	1	101	102	-16.4	-16.5	54552	2009	1813	16753		1063	9	
TSWC1-3	sphalerite	2	99	100	-16.4	-16.5	54301	2122		18093		1031	8	
TSWC1-3	sphalerite	3	118	119	-16.4	-16.5	50220	2418	2080	19906		1151	15	
TSWC1-3	sphalerite	4	101	102	-16.4	-16.5	53847	1805		17879		1074	15	145
TSWC1-3	sphalerite	5	101	102	-16.4	-16.5	58071	1776	2020	13675	372	1114	10	132
TSWC1-3	sphalerite	6	101	102	-16.4	-16.5	54213	2089	2573	16384	387	1126	14	220
TSWC1-3	sphalerite	7	101	102	-16.4	-16.5	52855	2043	3067	17465	755	955	17	296
TSWC1-3	sphalerite	8	101	102	-16.4	-16.5	54121	1629	1743	17858	583	872	10	214

* Th = homogenization temperature

** Tm = last ice melting temperature

Appendix III

LA-ICP-MS Elemental Composition Analyses of Sphalerite from Ozark MVT Deposits

Sample ID	Mineral	FI#	Fe ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm
NACP1-8	sphalerite	1	1119	22	664230	6395	4
NACP1-8	sphalerite	2	1115	11	663841	6836	1
NACP1-8	sphalerite	3	1010	91	664440	6177	21
NACP1-8	sphalerite	1	963	179	664913	5562	48
NACP1-8	sphalerite	2	951	100	664662	5964	50
NACP1-8	sphalerite	3	1001	141	664225	6333	69
NACP1-8	sphalerite	1	1036	89	664993	5495	12
NACP1-8	sphalerite	2	977	99	665652	4829	9
NACP1-8	sphalerite	3	999	73	664026	6707	12
NAPA1-13B	sphalerite	1	293	159	667171	3772	49
NAPA1-13B	sphalerite	2	299	114	667109	3934	30
NAPA1-13B	sphalerite	3	314	282	667173	3571	94
NAPA1-13B	sphalerite	4	352	608	666901	3368	190
NAEX1-8	sphalerite	1	1548	117	665379	4397	22
NAEX1-8	sphalerite	2	1403	158	663469	6291	53
NAEX1-8	sphalerite	1	1703	144	665074	4515	29
NAEX1-8	sphalerite	2	1695	151	664893	4735	33
NALD1-2	sphalerite	1	502	827	666213	3679	109
NALD1-2	sphalerite	1	375	9	666633	4553	
NAPA1-13	sphalerite	1	417	45	666576	4518	4
NAPA1-13	sphalerite	2	411	36	667137	3885	3
NAPA1-13	sphalerite	3	419	35	666205	4958	4
NAPA1-13	sphalerite	4	415	40	667014	3967	3
NACP1-8	sphalerite	1	987	17	664546	6174	4
NACP1-8	sphalerite	3	1009	18	663326	7534	9
NACP1-8	sphalerite	4	1042	19	664570	6086	5
NAPA1-13	sphalerite	1	453	8	666219	4897	
NAPA1-13	sphalerite	1	419	445	666052	4384	134
NAPA1-13	sphalerite	1	468	307	666145	4265	80
NAPA1-13	sphalerite	2	445	323	666515	4041	64
NAPA1-13	sphalerite	3	513	318	666854	3686	67
NAJP1-3	sphalerite	1	407	8	665428	5909	1
NAJP1-3	sphalerite	2	430	6	664938	6401	
NAJP1-3	sphalerite	4	431	9	664903	6423	
NAJP1-3	sphalerite	5	476	10	665265	5912	
NAJP1-3	sphalerite		388	6	665013	6416	
NAJP1-3o	sphalerite	1	627	197	667442	2996	15
NAMC1-1	sphalerite	1	880	150	666026	4448	17
NAMC1-1	sphalerite	2	1143	14	664030	6543	4
NAMC1-1	sphalerite	3	987	51	665054	5561	12
NAMC1-1	sphalerite	4	934	113	665531	4992	4
NAMC1-1	sphalerite	5	884	13	664396	6501	4
NAMC1-1	sphalerite	1	1109	95	662847	7725	46
NAMC1-1	sphalerite	2	1150	101	662311	8439	57

Sample ID	Mineral	FI#	Fe ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm
NAMC1-1	sphalerite	4	1048	89	661426	9447	86
NAMC1-1	sphalerite		1274	79	661803	8905	55
NAMC1-1	sphalerite		1417	97	662127	8358	6
NAEX1-7	sphalerite	2	744	229	667206	3037	15
NAEX1-7	sphalerite	1	752	80	667147	3313	12
NAEX1-7	sphalerite	1	1078	2	665367	5016	
NAEX1-7	sphalerite	2	1120	1	665306	5066	
NAEX1-7	sphalerite	3	1125	1	665327	5020	
NAEX1-7	sphalerite	4	1163	1	665409	4874	
NAEX1-7	sphalerite		886	1	666163	4373	
NAEX1-7	sphalerite		802	1018	667749	1463	5
NAEX1-7	sphalerite	1	905	162	667751	2257	5
NAEX1-7	sphalerite		949	44	667685	2458	1
NAEX1-7	sphalerite		896	27	668042	2140	1
NAEX1-7	sphalerite		1011	23	667659	2461	1
NACP1-8	sphalerite	1	1101	34	663148	7451	2
NACP1-8	sphalerite	2	1151	26	663353	7221	1
NACP1-8	sphalerite	1	1191	12	663519	6941	7
NACP1-8	sphalerite	2	1043	20	664498	5885	4
NACP1-8	sphalerite	4	1166	92	664339	5840	13
NAEX1-14	sphalerite	1	866	277	667645	2188	4
NAEX1-14	sphalerite	2	965	463	667633	1931	5
NAEX1-14	sphalerite	3	924	100	667275	2831	12
NAEX1-2	sphalerite	1	713	46	666948	3382	9
NAEX1-2	sphalerite	2	735	64	666816	3522	14
NAEX1-2	sphalerite	3	727	62	666997	3282	12
NAJP1-10	sphalerite	1	891	24	665230	5366	
NAJP1-10	sphalerite	2	881	34	664733	5865	1
NAJP1-10	sphalerite	3	804	29	664857	5894	1
NAJP1-10	sphalerite	4	842	46	664056	6711	
NAJP1-10	sphalerite	4	758	72	664159	6659	2
NAJP1-10	sphalerite	1	992	94	659735	11122	23
NAJP1-10	sphalerite	2	968	77	660436	10843	3
NAJP1-10	sphalerite	3	1028	33	663823	6751	1
NAJP1-10	sphalerite		1303	169	661351	8962	1
NAJP1-10	sphalerite		1201	174	661581	9030	1
NAJP1-10	sphalerite		1295	178	661519	9157	1
NAJP1-10	sphalerite		1363	108	663425	6794	10
NAJP1-10	sphalerite		760	246	667706	2453	4
NAJP1-10	sphalerite		750	209	667553	2702	8
NALB1-1	sphalerite	1	808	1	664164	6805	
NALB1-1	sphalerite	2	1080	1	663823	6851	
NALB1-1	sphalerite	3	878		663647	7314	
NALB1-1	sphalerite	1	457	16	665318	5846	1
NALB1-1	sphalerite	2	457	16	665318	5846	1
NALD1-4	sphalerite	4	397	451	667192	3116	63
NALD1-4	sphalerite		457	16	665318	5846	1
NALD1-4	sphalerite		390	418	667278	3145	59
NAMC1-1	sphalerite	1	1488	38	660860	9695	12

Sample ID	Mineral	FI#	Fe ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm
NAMC1-1	sphalerite	2	1526	80	659234	11365	15
NAMC1-1	sphalerite	3	1784	98	660751	9401	14
NAMC1-1	sphalerite	4	1607	42	660136	10373	11
NAMC1-1	sphalerite	6	1765	132	660242	9993	19
NAMC1-1	sphalerite		1343	194	660450	10108	2
NAMC1-1	sphalerite		1359	203	660408	10222	2
NAMC1-1	sphalerite		1663	113	661188	9072	11
NAMC1-1	sphalerite		1702	120	661048	9179	10
NAMC1-1	sphalerite		1150	192	663960	6356	31
NAMC1-1	sphalerite		1040	152	664491	5920	17
NAMC1-1	sphalerite	1	1008	46	665051	5443	11
NAMC1-1	sphalerite	2	943	21	664590	6092	3
NAMC1-1	sphalerite	1	1227	17	663752	6727	1
NAMC1-1	sphalerite	2	1456	52	661757	8673	19
NAMC1-1	sphalerite	3	1524	31	660397	10244	24
NAMC1-1	sphalerite	4	1711	25	659989	10484	19
NAMC1-1	sphalerite	2	1070	91	663476	7094	44
NAMC1-1	sphalerite	3	1116	60	662961	7698	25
NAMC1-1	sphalerite	4	1363	21	662119	8410	11
NAMC1-1	sphalerite	5	1011	10	663695	7048	6
NAMC1-1	sphalerite	2	1839	144	660087	10108	11
NAMC1-1	sphalerite	3	1865	224	659889	10176	17
NAMC1-1	sphalerite	4	1741	166	661078	8953	7
NAMC1-1	sphalerite	5	1699	155	660531	9689	7
NAMC1-1	sphalerite	6	1755	188	661326	8661	4
NAMC1-1	sphalerite	7	1844	145	659845	10293	7
NAMC1-1	sphalerite	8	1755	188	661326	8661	4
NAPA1-13	sphalerite	1	517	452	666201	4101	112
NAPA1-13	sphalerite	2	544	445	665956	4358	111
NAPA1-13	sphalerite	3	544	445	665956	4358	111
NAPA1-13	sphalerite	5	570	465	665641	4646	148
NAPA1-13	sphalerite	6	553	417	665790	4600	133
NAPA1-13	sphalerite	7	541	435	665671	4708	151
NAPA1-13	sphalerite	1	467	94	666365	4502	23
NAPA1-13	sphalerite	2	568	307	665091	5477	189
NAMC1-1	sphalerite	1	1352	125	662860	7453	7
NAMC1-1	sphalerite	3	1442	123	662022	8370	4
NAMC1-1	sphalerite	4	1346	129	661850	8744	4
NAMC1-1	sphalerite	5	1496	129	662274	8018	9
NAMC1-1	sphalerite	6	1479	125	662199	8085	9
NAMC1-1	sphalerite	7	1475	105	662008	8376	12
NAMC1-1	sphalerite	8	1557	127	662033	8162	14
NAPA1-13	sphalerite	1	623	5	664420	6657	
NAPA1-13	sphalerite	1	566	16	663126	8046	17
NAPA1-13	sphalerite	2	511	5	663861	7404	
NAPA1-13	sphalerite	3	429		663536	7723	1
NAPA1-13	sphalerite	1	500	363	665618	4766	140
NAPA1-13	sphalerite	2	311	268	665200	5749	167
NAPA1-13	sphalerite	3	544	332	665666	4745	133

Sample ID	Mineral	FI#	Fe ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm
NAPA1-13	sphalerite	4	518	338	665564	4842	130
NALD1-2	sphalerite	1	265	307	667090	3473	30
NALD1-2	sphalerite	2	162	278	666524	4323	40
NALD1-2	sphalerite	1	159	57	665675	4948	32
NALD1-2	sphalerite	2	333	100	667144	3561	24
NALD1-4	sphalerite	1	382	356	667060	3361	59
NALD1-4	sphalerite	2	332	293	666623	3837	57
NALD1-4	sphalerite	4	435	4	665713	5548	1
NALD1-4	sphalerite		426	4	665988	5133	1
NAPA1-13	sphalerite	1	375	4	664609	6754	3
NAPA1-13	sphalerite	3	407		664621	6800	1
NAPA1-13	sphalerite	1	289	79	666161	4910	16
NAPA1-13	sphalerite	2	263	96	665933	5059	27
NAPA1-13	sphalerite	4	229	103	664764	6550	28
NAPA1-1	sphalerite	1	625	333	666446	3830	65
NAPA1-1	sphalerite	3	650	339	666246	4006	71
NAPA1-1	sphalerite	4	591	304	666107	4218	78
NACP1-8	sphalerite	2	1164	3	663322	6970	
NACP1-8	sphalerite	3	1029	1	663220	7248	
NACP1-8	sphalerite	1	1081	51	665184	5041	2
NACP1-8	sphalerite	2	1125	18	663600	6880	
NACP1-8	sphalerite	3	983	193	665959	3962	4
NACP1-8	sphalerite	4	992	97	664345	5978	3
NAEX1-2	sphalerite	1	806	214	665631	4319	76
NAEX1-2	sphalerite	2	848	221	665575	4347	76
NAEX1-2	sphalerite	3	734	181	665958	4131	63
NAEX1-2	sphalerite	1	613	95	667214	3157	19
NAEX1-2	sphalerite	2	597	72	667397	2964	9
NAEX1-2	sphalerite	3	687	50	667248	3103	6
NAEX1-2	sphalerite	1	649		664576	6246	
NAEX1-2	sphalerite	2	771	1	664903	5760	1
NAEX1-2	sphalerite	3	785	2	664566	6122	
NAEX1-2	sphalerite	4	638		663978	6925	1
NAEX1-7	sphalerite	1	1236	1	665058	4983	
NAEX1-7	sphalerite	2	990		664705	5669	
NAJP1-3	sphalerite	1	685	11	663111	7926	
NAJP1-3	sphalerite	2	562	22	662318	8913	1
NALD1-4	sphalerite	7	414	5	666442	4426	1
NALD1-4	sphalerite	8	368	8	665964	4963	6
NALD1-4	sphalerite	9	397	12	666286	4572	8
NALD1-4	sphalerite	10	393	14	665744	5137	5
TSBS3-2	sphalerite	2	1489	497	665409	3982	25
TSBS3-2	sphalerite	3	1393	621	665321	4054	21
TSBS3-2	sphalerite	5	1715	308	663903	5675	31
TSBS3-2	sphalerite	6	1421	610	666185	3017	9
TSBS3-2	sphalerite	7	1337	704	666555	2614	4
TSBS3-2	sphalerite	8	1095	733	667120	2243	2
TSBS3-2	sphalerite	9	1277	605	666000	3451	14
TSBS3-2	sphalerite	10	1588	375	665401	4031	16

Sample ID	Mineral	FI#	Fe ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm
TSBS3-2	sphalerite	1	1360	236	667843	1661	
TSBS3-2	sphalerite	2	1284	253	667846	1730	
TSBS3-2	sphalerite	1	1289	246	667940	1628	
TSBS3-2	sphalerite	2	1354	269	668126	1069	
TSBS3-2	sphalerite	3	1371	196	668252	1197	
TSBS3-2	sphalerite		1201	229	668168	1487	
TSBS3-2	sphalerite		1664	654	667305	1419	
TSNC1-1	sphalerite	4	816	966	667278	2047	3
TSNC1-1	sphalerite	5	868	989	667570	1612	2
TSNC1-1	sphalerite	6	893	1028	667439	1631	1
TSNC1-1	sphalerite		1318	166	666639	3184	4
TSNC1-1	sphalerite		941	649	668015	1494	1
TSDW2-8	sphalerite	1	928	9	662288	8893	
TSDW2-8	sphalerite	2	864	10	662949	8203	2
TSDW2-8	sphalerite	1	1111	12	662047	8934	1
TSDW2-8	sphalerite	2	1111	13	662109	8859	1
TSDW2-8	sphalerite	1	1031	7	661943	9170	1
TSDW2-8	sphalerite		1496	68	659680	11140	3
TSDW2-8	sphalerite	1	861	405	664916	4972	39
TSDW2-8	sphalerite	1	890	5	663537	7409	
TSDW2-8	sphalerite	1	765	505	665638	4599	45
TSBS5-2	sphalerite	1	1297	147	665234	4530	4
TSBS5-2	sphalerite	3	3031	3	663374	4889	1
TSBS5-2	sphalerite	4	2879		662735	5837	1
TSCM2-1	sphalerite	2	1449	72	663199	6851	5
TSCM2-1	sphalerite	3	1417	66	663324	6864	4
TSCM2-1	sphalerite	4	1486	20	662625	7620	4
TSCM2-1	sphalerite	1	1350	24	662627	7846	7
TSCM2-1	sphalerite	2	1417	48	662284	8077	21
TSCM2-1	sphalerite	4	1505	44	662731	7494	17
TSCM2-1	sphalerite	1	1275	531	665764	3677	51
TSCM2-1	sphalerite	2	1370	488	665669	3705	47
TSCM2-1	sphalerite	3	1436	527	665611	3607	57
TSDW2-8	sphalerite	1	1375	12	661358	9351	
TSDW2-8	sphalerite	2	1438	11	660958	9729	
TSDW2-8	sphalerite	3	1388	17	661122	9634	
TSDW2-8	sphalerite		1407	19	661810	8784	
TSDW2-9	sphalerite	1	1349	2	662753	7649	
TSDW2-9	sphalerite	2	1275	4	662872	7774	1
TSDW2-9	sphalerite	3	1349	2	662753	7649	
TSDW2-9	sphalerite	4	1342		662859	7695	1
TSDW2-9	sphalerite	5	1262	5	662924	7643	1
TSDW2-9	sphalerite		1334	3	662899	7629	
TSGY2-3	sphalerite	1	1453	144	665591	4145	37
TSGY2-3	sphalerite	2	1556	138	665901	3695	29
TSGY2-3	sphalerite	3	1592	158	665429	4182	35
TSPC2-1	sphalerite	1	2366	10	662042	7306	2
TSPC2-1	sphalerite	2	2282	11	661974	7497	3
TSPC2-1	sphalerite	4	2142	10	662248	7359	2

Sample ID	Mineral	FI#	Fe ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm
TSPC2-1	sphalerite	5	2322	19	661828	7591	8
TSPC2-1	sphalerite	6	2196	14	662050	7505	3
TSPC2-1	sphalerite	1	1790	30	664485	5142	4
TSPC2-1	sphalerite	6	1277	19	665120	5138	5
TSOR2-3	sphalerite	1	2105	264	664844	4087	27
TSOR2-3	sphalerite	2	2031	360	665302	3551	16
TSPC2-1	sphalerite	1	1206	809	667472	1536	1
TSPC2-1	sphalerite	2	1206	809	667472	1536	1
TSPC2-1	sphalerite	3	721	558	666850	2720	16
TSPC2-1	sphalerite	1	879	649	667652	1833	1
TSPC2-1	sphalerite	2	1233	581	667325	1323	1
TSPC2-1	sphalerite	1	2167	139	663479	5772	18
TSPC2-1	sphalerite	2	2074	132	663258	6128	24
TSPC2-1	sphalerite	3	2398	98	662184	7033	17
TSTR1-7	sphalerite	1	1672		663209	6774	
TSTR1-7	sphalerite	3	1324		663294	7178	1
TSTR1-7	sphalerite	4	1752		662759	7249	
TSTR1-7	sphalerite	5	1805	3	662975	6888	1
TSTR1-7	sphalerite	6	2165	2	662021	7600	
TSTR1-7	sphalerite	7	1869		662684	7138	
TSTR1-7	sphalerite	8	2115	2	662493	7101	
TSTR1-7	sphalerite	9	1693		663279	6737	
TSTR1-7	sphalerite	10	1577	3	663337	6828	
TSTR1-7	sphalerite	11	1658		663082	7077	
TSTR1-7	sphalerite	12	1527	2	662868	7488	1
TSWB3-9	sphalerite	1	1871	30	664353	5215	2
TSWB3-9	sphalerite	2	1950	23	664498	4990	1
TSWB3-9	sphalerite	6	1821	21	664313	5340	2
TSWB3-9	sphalerite	8	1854	21	664471	5140	2
TSWB3-9	sphalerite	9	1776	16	665052	4544	1
TSWB3-9	sphalerite	12	1837	19	664530	5075	1
TSBS5-2	sphalerite	1	1635	1	664313	5434	
TSBS5-2	sphalerite	2	1569		663407	6589	
TSBS5-2	sphalerite	1	1791	6	663379	6325	1
TSBS5-2	sphalerite	2	1722	12	662997	6817	3
TSBS5-2	sphalerite	3	1462	185	666263	2983	4
TSBS5-2	sphalerite	1	1415		664061	6009	
TSBS5-2	sphalerite	2	1483		664511	5323	
TSBS5-2	sphalerite	3	1478	1	664979	4883	
TSBS5-2	sphalerite	4	1440		664450	5498	
TSBS5-2	sphalerite	5	1619		664047	5721	
TSBS5-2	sphalerite	1	1554		663657	6242	1
TSBS5-2	sphalerite	2	1670		663328	6496	
TSBS5-2	sphalerite	3	1714		663393	6368	1
TSBS5-2	sphalerite	4	1475		663448	6547	1
TSBS5-2	sphalerite	5	1211		663526	6749	1
TSBS5-2	sphalerite	6	1520		663934	6054	
TSCM2-1	sphalerite	1	2483	47	658067	11529	1
TSCM2-1	sphalerite	2	1904	35	659311	10907	

Sample ID	Mineral	FI#	Fe ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm
TSCM2-1	sphalerite	3	2073	23	659812	10153	
TSCM2-1	sphalerite	4	2697	76	657274	12274	
TSCM2-1	sphalerite	5	2756	36	659205	9956	
TSCM2-1	sphalerite	6	2551	30	659198	10283	1
TSCM2-1	sphalerite	7	2624	32	659055	10268	1
TSCM2-1	sphalerite	2	2597	33	658771	10595	1
TSCM2-1	sphalerite	3	2362	7	659941	9592	
TSCM2-1	sphalerite	4	2443	21	659773	9655	1
TSCM2-1	sphalerite	1	2212	29	661933	7478	1
TSCM2-1	sphalerite	3	2198	13	661496	7991	
TSCM2-1	sphalerite	5	2291	19	660436	9080	1
TSNC1-2	sphalerite	1	1496	38	665182	4496	2
TSNC1-2	sphalerite	2	1471	34	665022	4670	2
TSNC1-2	sphalerite	3	1462	40	665024	4684	2
TSNC1-2	sphalerite	4	1429	35	665054	4734	3
TSNC1-2	sphalerite	5	1341	32	664956	4911	2
TSNC1-2	sphalerite	6	1447	21	664567	5275	1
TSNC1-2	sphalerite	7	1463	22	665491	4272	1
TSNC1-2	sphalerite	8	1378	18	665284	4547	1
TSNC1-2	sphalerite	1	1343	282	665562	3820	34
TSNC1-2	sphalerite	2	1157	299	665649	3919	34
TSWB3-9	sphalerite	1	2226	137	661909	7232	33
TSWB3-9	sphalerite	2	2378	131	661398	7654	36
TSWB3-9	sphalerite	4	2371	144	661689	7322	31
TSWB3-9	sphalerite	5	2310	135	661708	7368	33
TSWB3-9	sphalerite	7	2165	131	662122	7058	33
TSTR1-7	sphalerite	1	1952	2	662575	7112	
TSTR1-7	sphalerite	2	1872	1	662480	7303	
TSTR1-7	sphalerite	5	1808		662225	7653	
TSTR1-7	sphalerite	6	1691		662778	7148	1
TSTR1-7	sphalerite	7	1772		662272	7682	
TSTR1-7	sphalerite	8	1799		662186	7709	
TSTR1-7	sphalerite	9	1637		662305	7787	
TSTR1-7	sphalerite	10	1631		662398	7641	
TSTR1-7	sphalerite	11	1767		663492	6379	
TSTR1-7	sphalerite	12	1610		663636	6423	
TSTR1-7	sphalerite	13	1356	4	663506	6902	1
TSTR1-7	sphalerite	14	1809		663439	6396	
TSTR1-7	sphalerite	15	1695		663054	7022	
TSTR1-7	sphalerite	17	1755		662970	7054	
TSWC1-3	sphalerite	1	2962		660658	8062	1
TSWC1-3	sphalerite	4	2746	3	661029	7912	
TSWC1-3	sphalerite	5	2869		660806	8010	
TSWC1-3	sphalerite	8	2338		661711	7658	
35_8V22	sphalerite	1	2072	6	660562	9212	10
35_8V22	sphalerite	2	601	67	665121	5751	9
35_8V22	sphalerite	1	15486	140	645969	6650	2893
35_8V22	sphalerite	1	2125	78	662039	6770	24
35_8V22	sphalerite		2581	40	660382	8715	16

Sample ID	Mineral	FI#	Fe ppm	Cu ppm	Zn ppm	Cd ppm	Pb ppm
35_8V22	sphalerite	2	1916	41	662664	7040	15
35_8V22	sphalerite	3	2043	42	662926	6677	14
WF2	sphalerite	1	1148	69	658900	12473	11
WF2	sphalerite	3	813	93	665178	5234	24
WF2	sphalerite	1	3053	6	652922	16836	30
MAG13	sphalerite	1	253	13	665104	6239	1
MAG13	sphalerite	3	295		666313	4870	1
MAG13	sphalerite	1	2911	358	660887	7439	38
MAG13	sphalerite	1	743	24	667445	2819	1
MAG13	sphalerite	2	620	204	667860	2117	1
MAG13	sphalerite	3	993	134	667349	2114	1
MAG13	sphalerite	4	1035	168	667382	2262	2
MAG13	sphalerite	1	1828	129	665706	3131	1
MAG13	sphalerite	2	3485	66	663797	3547	
MAG13	sphalerite	1	708	211	667588	2459	3
MAG13	sphalerite	2	825	155	667582	2496	2
MAG13	sphalerite	3	1169	10	663679	6972	1
VTW2	sphalerite	1	5211	1659	647261	16715	1277
MAG13C	sphalerite	1	4432		661387	5363	
MAG13A	sphalerite	1	4514	1	661202	5482	
MAG13A	sphalerite	2	4684		661043	5399	
MAG13A	sphalerite	3	5039	5	660980	5025	2
MAG13A	sphalerite	4	5352		660678	4998	1
MAG13A	sphalerite	5	4553	3	661526	5101	1
MAG13A	sphalerite	1	4006		660986	6379	1
MAG13A	sphalerite	4	4258		660633	6425	1
MAG13B	sphalerite	1	1875	174	666598	2145	2
MAG13B	sphalerite	2	3575	222	664343	2597	
MAG13C	sphalerite	1	10822	52	655355	4302	107
VTW2E	sphalerite	1	2069	740	657842	11140	236
VTW2E	sphalerite	4	3568	920	655275	11909	328
VTW2E	sphalerite	1	2264	508	662454	5766	163
WF2B	sphalerite	1	1635	133	664144	5481	28
WF2B	sphalerite	2	1541	39	663842	6001	10
WF2B	sphalerite	3	1858	173	662709	6813	44
WF2B	sphalerite	4	1871	212	664104	5121	61