Lead Isotope Dating of Galena Artifacts from Florida

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Abstract

Galena artifacts samples from Florida were analyzed for their lead isotopic ratios. These ratios will lead to a conclusion of their geographic origination once the research is complete. The geographic region was narrowed between three surface galena deposits readily accessible to Indians in the areas. These three deposits consist of the Upper Mississippi River Valley, Southeast Missouri, and the Tri-State region of Oklahoma, Kansas, and Missouri. Samples of galena artifacts include those from the Florida Bureau of Archaeological Research and Harley Means from Miami Circle, Oak Knoll, Lake Jackson Mound, Block Sterns, and Wassica River. The information from this data will help determine Indian trade routes to Florida.

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I. INTRODUCTION

Objective

Galena artifacts samples from Florida were analyzed for their lead isotopic ratios. These ratios will lead to a conclusion of their geographic origination. The geographic region was narrowed between three surface galena deposits readily accessible to Indians in the areas. These three deposits consist of the Upper Mississippi River Valley, Southeast Missouri, and the Tri-State region of Oklahoma, Kansas, and Missouri. The information from this data will help determine Indian trade routes to Florida.

Sample Locations

Galena artifacts are found throughout the United States, as seen in Figure 1. For this study, eleven samples in total were obtained for evaluation of lead isotope ratios. Ten of the eleven were obtained from the Florida Bureau of Archaeological Research. One more was obtained from Harley Means who discovered it in a spring off the Wassica River.

Of the ten, four are from the Miami Circle on Brickell Point off the Miami River. Another two are from Lake Jackson Mound north of Tallahassee, Florida. Another sample is from Block Sterns. The last three samples are from Oak Knoll. See the Appendix for more detailed information regarding the identity and location of the sample data.

Of these eleven samples ten are from Indian Mounds. Often these mounds were middens, which is the trash pile some Native Americans in the region used to discard objects. Some of the artifacts found were galena bird effigies and beads.

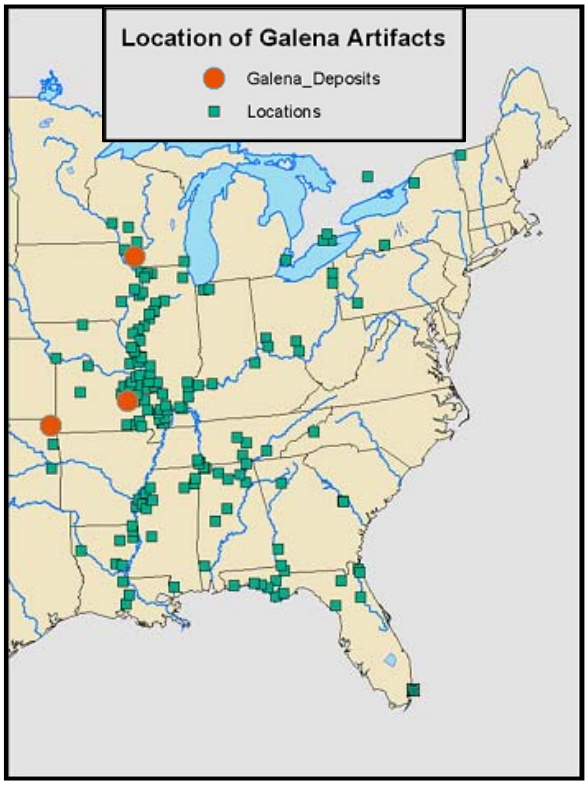

Figure 1. Galena artifacts throughout US.

In the Miami Circle area, Tequesta Indians occupied the area around 2000 years ago. They were one of the first Native American tribes to permanently settle in Florida. The Miami Circle is embedded in solid rock and is 38 ft in diameter. The age of the Miami Circle is still under study.

II. THEORY

Galena

Galena is one of the more common rocks for collection. Its silvery-lead color and luster makes an easy distinction from other minerals. Pure galena is made up of 86.6% lead and 13.4% sulfur. Galena is also known as lead sulfide, plumbous sulfide, lead (II) sulfide, lead monosulfide, and lead sulfide. Galena can contain 1% silver, thus making it the major ore mined for both lead and as a byproduct, silver. For the galena used, the consistency was 87% lead and

13% sulfur. Galena is found in two shapes: cubic and octahedral. These two forms can be found on the same mineral when the conditions change in the ore forming solution.

Lead has been around for many years. The element obtained its name from the Latin name "plumbum," hence the element symbol for lead is Pb. Lead is the primary element found in galena. Lead is poisonous and was previously used in many applications until this discovery.

Lead Isotope Ratios

Lead has three radiogenic isotopes: ^{208}Pb, ^{207}Pb, and ^{206}Pb. One non-radiogenic isotope is ^{204}Pb. These isotopes decay from different parents. 232-thorium decays to 208-lead, 235-uranium decays to 207-lead, and 238-uranium decays to 206-lead.

$$^{232}\text{Th} \rightarrow {}^{208}\text{Pb}$$
$$^{235}\text{U} \rightarrow {}^{207}\text{Pb}$$
$$^{238}\text{U} \rightarrow {}^{206}\text{Pb}$$

In concern of the isotope source variation of radiogenic leads, the amount of a lead isotope found in an area is the composition of the initial lead isotope plus that derived from radioactive decay.

$$^{207}Pb_{today} = {}^{207}Pb_O + ({}^{235}U \rightarrow {}^{207}Pb)$$
$$^{206}Pb_{today} = {}^{206}Pb_O + ({}^{235}U \rightarrow {}^{206}Pb)$$
$$^{208}Pb_{today} = {}^{208}Pb_O + ({}^{232}Th \rightarrow {}^{208}Pb)$$

These three isotopes can be put into ratios with 204-lead whose concentration does not change with time. 207 and 208 lead isotopes are also compared to 206 lead to give a little more information.

Geographic Identity

A geographic region has a lead isotope identity. Once the region has been sampled for lead isotope concentration of galena that concentration will not change because there is no uranium in galena. When comparing three lead isotope ratios the area will be unique among these ratios. The origination of galena from that geographic area should be possible.

Higher uranium content in an area will yield a higher radiogenic lead content. The isotopic evolution of lead results from the decay of uranium and thorium. Distinct patterns occur from the lead isotopic abundances associated with the specific environment. Thus, chemical differences arise between sources. Selective leaching in the Mississippi Valley ore deposits lead to a very radiogenic type of lead.

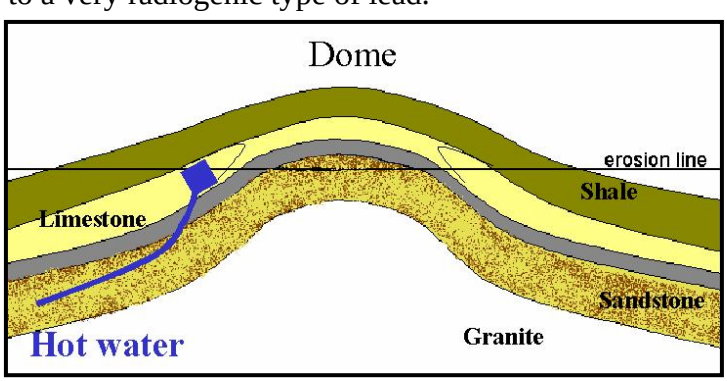

Figure 2. Inland Sedimentary layers.

As seen from Figure 2, the inland sedimentary layers aid in the development of galena. In the southeast Missouri district, the Ozark Dome is a prime example of this occurrence. Hot water runs in between the granite and shale layers, which are impenetrable by the liquid. With the

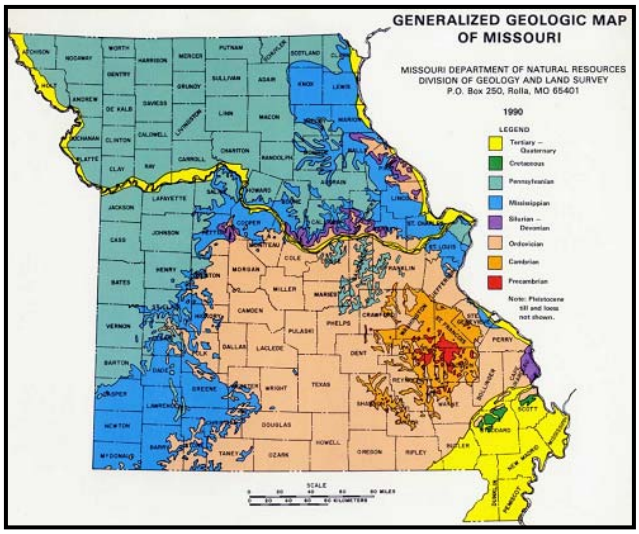

Figure 3. Southeast Missouri Ozark Dome.

help of erosion and the dome, the liquid becomes trapped and galena begins to from in the area with the right ore composition. The erosion effect contributes to the onion layered look in Figure 3 found in the Southeast Missouri district. The red and orange represent the area of the Ozark Dome.

The formation of geographic identity is further explained in Figure 4. From the beginning of the formation of the earth a certain amount of uranium was within the crust. The departure about 1 billion years ago along geographic regions can explain the higher uranium to lead ratios.

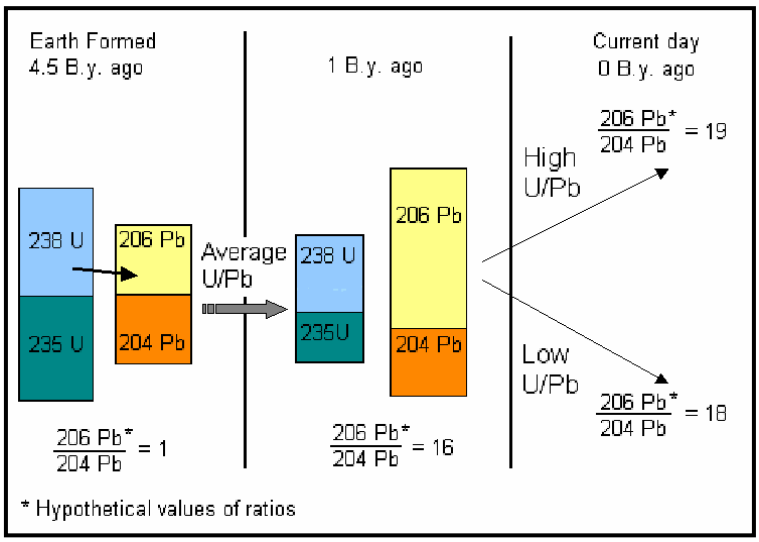

Figure 4. Isotope Geographic Identity Figure.

The net change in lead isotopic ratios (relative to ^{204}Pb) is dependent upon the relative ratio of uranium to lead in the material and not the absolute concentrations of uranium. The anomalous high uranium to lead ratio leads to higher lead isotopic ratios in galena. This type of galena is named J-Type for Joplin Missouri where it was first documented.

III. EXPERIMENTAL PROCEDURE

Galena has a high lead content and thus does not need to be run through any ion exchange columns. The procedure for testing the lead isotopic ratios is rather simplistic.

Galena is sized using a stereoscope and geometric assumptions made as to whether the shape is cubic or octahedral. All samples in this study were assumed cubic. The average size was 0.2 mm in length containing approximately 0.306 μg of lead.

Using very clean Teflon beakers, the galena is then dissolved in 7N clean nitric acid (HNO3) solution. This allows the lead to become ions in the solution while the sulfur precipitates out to form a small white spot. Small plastic syringes were then used to separate the solution from the sulfur precipitate. After measuring out the proper volume for 60ng of lead, the samples were then treated with clean hydrobromic (HBr) acid to break down the nitrates created.

The samples were then evaporated to dryness. A 0.25N nitric solution was then added to the evaporated sample beakers. A weak phosphoric acid and a silica gel were also added before loading the samples. Single rhenium filaments were used to test the samples in the thermal ionization mass spectrometer (TIMS). The filaments were loaded with the samples. A 1 μL in the same spot contained approximately 60 ng of lead sample. These loaded filaments were then loaded onto the magazine to test in the mass spectrometer. The magazine can hold only 13 filaments.

One type of mass spectrometer was used the Thermal Ionization Mass Spectrometer (TIMS), Finnigan 626. This uses heat to create ions from the samples on the filaments. These ions then go through the magnet in the mass spectrometer. It differentiates the heavier ions from the lighter ones capable of discerning the different isotopes. The computer output is given on the masses of the isotopes of lead. The output should be reproducible and accurate.

IV. RESULTS

The results have not been tabulated yet. Research is still being conducted to obtain enough reference data on geographic variations of lead isotopes. The sample data will then be compared to the geographic isotope data. The current geographic variation is in Figure 5.

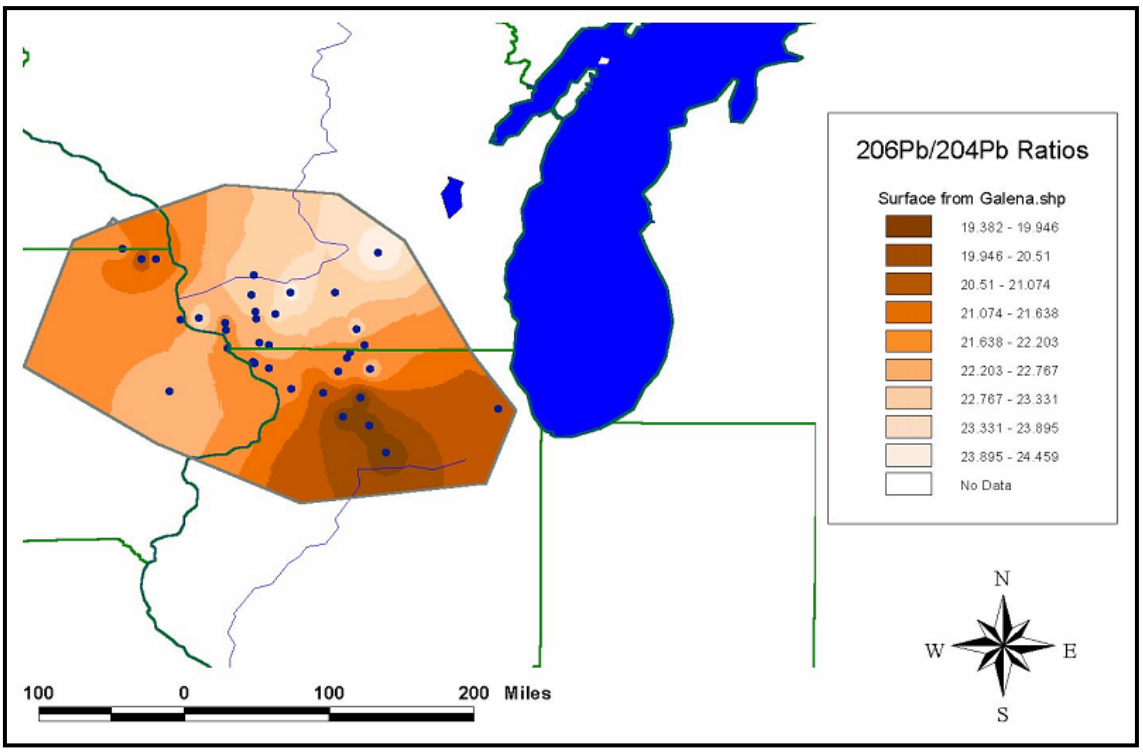

Figure 5. Upper Mississippi River Valley Lead Isotope Variation.

V. DISCUSSION

Using an example from Austin's "Isotope Analysis of Galena from Prehistoric Archaeological Sites in South Florida," Figure 6 gives information similar to those expected from this experiment's samples of galena.

Site Name Samples in FL	206Pb 204Pb	207Pb 206Pb	208Pb 204Pb	208Pb 206Pb
Royce Mound	21.802	0.7320	40.93	1.878
Fort Center's, Mound A	21.867	0.7306	41.04	1.876
Brown's Mound, Pineland	22.005	0.7261	41.01	1.863

Figure 6. Artifacts Lead Isotope Ratios.

Using the geographic isotopic identity, the origination location of the galena can be narrowed to a specific location. The ratio of ^{206}Pb to ^{204}Pb in Figure 6 are compared to those of geographic variation in Figure 5. All three would fall in the 21.638 to 22.203 range represented by the bright orange color. The exact location would be narrowed down using the other lead isotope ratios and the geographic isotope variation.

If by using the Thermal Ionization Mass Spectrometer (TIMS) the results do not pinpoint to a specific location. The samples will be reanalyzed using the Secondary Ionization Mass Spectrometer (SIMS), ISOLAB MS. This mass spectrometer uses an initial ion stream to create a secondary ion stream of sample particles. The results are more precise and accurate than the TIMS; however the machine is more prone to breaking down. The SIMS could possibly identify if samples came from the same original "parent" piece of galena.

Some potential problems exist throughout the experiment. The chemistry without the ion exchange columns may introduce errors in isotopic measurements. Another may e the overlapping ratio identities of the geographic regions. This may be reduced with more information.

Temporary setbacks have prevented the research from being completed within the eight weeks of the internship. Finding resources with both latitude and longitude coordinates of samples and lead isotopic ratios has been a key component in the delay of the project. A database of isotopic ratios has been found but we are still waiting for delivery. The database is composed of all geographic data taken before 1979 on lead isotopes. The lab also ran out of rhenium filaments to test lead isotopes so a shipment has delayed the continuation of the research.

VI. CONCLUSION

Further research will occur depending on funding of the project and time available to complete it. Resources will continue to be hunted until the database comes in.

VII. REFERENCES

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The Miami Circle, Biscayne National Park http://www.nps.gov/bisc/miamicircle.htm. http://www.nps.gov/bisc/images/miamicircle2.jpg. Images courtesy of Miami-Dade County Historic Preservation Division. July 22.

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VIII. APPENDIX

Equipment
11 samples
11 5mL clean Teflon beakers
12 7mL clean Teflon beakers
11 20mL clean Teflon beakers
cleaned syringes in 1:1 HNO3 left in DI
single Re filaments
DI or QDI
Stereoscope, mm ruler

Sample Data Numbers
HMA
MC1A (8DA12) BAR.1.127.1
MC1B
MC2A (8DA12) MDC.1.412.7
MC2B
LJ1 FBAR #96A.115.41.1
LJ2 FBAR #96A.115.41.2
OK1A LL729.539.1
OK1B
OK2 LL729.539.2
BS1 (8LE148) FBAR #94.68.322.11