

# Isotopic Insights: Show Me the Money

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**T**his talk will focus on two general techniques that I've been developing for the past thirteen years.

I'm trying to figure out how we can know where to find specific types of metals in the earth's crust.

I will focus in on three topics: gold deposits in South Africa, copper, and using copper isotopes to trace metals in archeological artifacts. This talk will be a summary and sort of interpretive, without providing the details of each technique.

The first technique uses Re-Os isotopes. You can use these radiogenic isotopes, which decay with time, to determine the age and origin of gold. The second technique uses transition metal isotope fractionation. You can use these copper isotopes to identify low-temperature processes and to fingerprint artifacts.

So first we're going to look at the gold occurrence in the Witwatersrand Basin in South Africa. This area contains the largest gold occurrence on earth and the largest underground mine workings that exist. In fact, about 40% of the gold on earth comes from this deposit. The rocks lie in a basin that is part of the largest continuous rock unit of the oldest exposed rocks on earth. The gold is contained here in the 2.7 billion year old rock. When I visited some of these deposits, I traveled to some of the deepest and oldest points in the earth that a human could be. I was contacted by Anglo Gold, to analyze the gold deposits here. The question I was trying to address for the company was, "How did the gold get there in the first place?" This is important because if you have an understanding of how the gold got there, then you can figure out where more of it might be. In order to find out how the gold got there, you need to understand when it was introduced into the basin and where it originated.

There are three models that describe how the gold was introduced into the basin. First, is the "Unmodified Placer" model where the gold (Au) was weathered from an igneous rock and transported into the basin, such as what happened with the California Gold Rush. Mineralization in this model is thought to have occurred in an analogous process. In this model the source of the gold is older than the age of the rocks. Many people think that this unmodified placer model is the correct answer.

The second model shows that the gold wasn't introduced before the rock was deposited; it was actually introduced afterward. This is termed the "Hydrothermal Au Model." In this model you basically had this basin that was buried and through some event, gold was added to the crust. If that is the case, then mineralization would have happened post 2.7 billion years ago. Of course in geology, you waffle and

say, “Oh, it’s a bit of this and a bit of that.” And that’s what the third model, the “Modified Plaser Model” is, a combination of the other two models. -- Here, the gold comes from older source rocks and then fluids are introduced, adding more hydrothermal gold on top of the plaser. When these two events occur, this makes a large gold deposit.

Another question is looking for copper isotope fractionation in porphyry copper mines. How did the mine get enriched in copper? It’s basically a similar question to what I did in the gold mines, but it’s a different type of mine that I used.



Figure 1: Cu Isotopes – Similar Question of How Did the Cu Get Enriched

In porphyry copper deposits, copper comes from a large, low grade ore body. We actually mine away and strip away a ton of rock and then we’re able to extract copper from that rock with a very low concentration and do it in an economic way.

This place I worked in is called Chuquibambilla, in Chile (Figure 1). This is a mile deep pit. You can see this thing from space. Two hundred and forty ton trucks move ore

The question I try to figure out is, “How does the copper concentrate to become economically viable?”



Figure 2: Large Low Grade Ore Bodies

This is the mineral chalcocite which appears as the dark colored streaks in Figure 2.

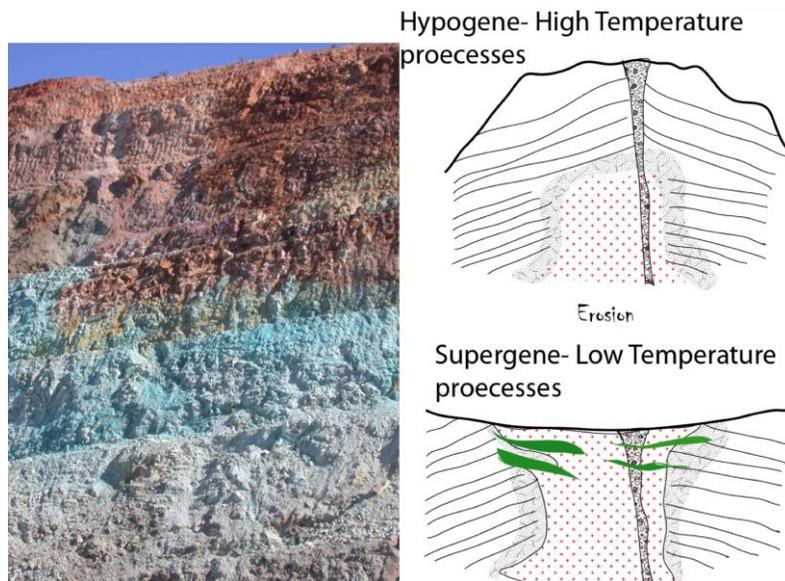


Figure 3

How do these deposits form? Figure 3, which represents the innards of a volcano, depicts the general processes that occur in these systems. In general there are two processes:

1. *High temperature process (listed as Hypogene—High Temperature process in Figure 3).* In the cross section the volcano has a depth of 3Km. The magma releases a fluid, which I'm

showing in this stipple pattern. It has a lot of copper and iron in it. The copper and iron minerals precipitate out copper sulfide and iron sulfide. Therefore, these rocks contain the minerals that we're interested in.

2. *Weathering and erosion process (listed as Supergene—Low Temperature process in Figure 3).* Over time these mountains weather and erode away. I've shown in the bottom portion of Figure 3 this process where you strip away all the shallow volcanic rocks and you then expose all the innards. When you expose these sulfide minerals that were once in the hypogene by this supergene process you create an acid mine drainage process where pyrite goes into solution to make acidic waters, like you have at Sky Top in State College. The weathering process serves to enrich the copper into greater and greater degrees in lower portions of the crust.

One of the questions that I'm trying to figure out are, "When we look at some sort of chemical signature in these leech rocks, can that lead us to figuring out where all the copper is underneath?"

We know there are lots of areas in the earth that are covered with rocks at the surface with iron oxides in them or oxidized iron in them but that don't have copper at depths. So the question is, how can we use what we have at the surface to detect or figure out what we have underneath, like in Figure 3? This is a big problem in many of these ore deposits. Figure 4 addresses this issue.



Figure 4

This is just a closer image of leached rocks. We have many rocks on the earth's surface that look leached and have iron oxides in them that indicate the presence of this low temperature process that I talked about with weathering. But we don't know if there is copper at depth.

The technique I use measures the two isotopes of copper. The value that you'll see in the next couple slides is the delta 65Cu. This means that you have this ratio of 65/63 copper isotopes and at high temperature in most natural rocks, you don't see any variation or values near 0. If you have some sort of low temperature process, what happens is that either 65 or 63 fractionates.

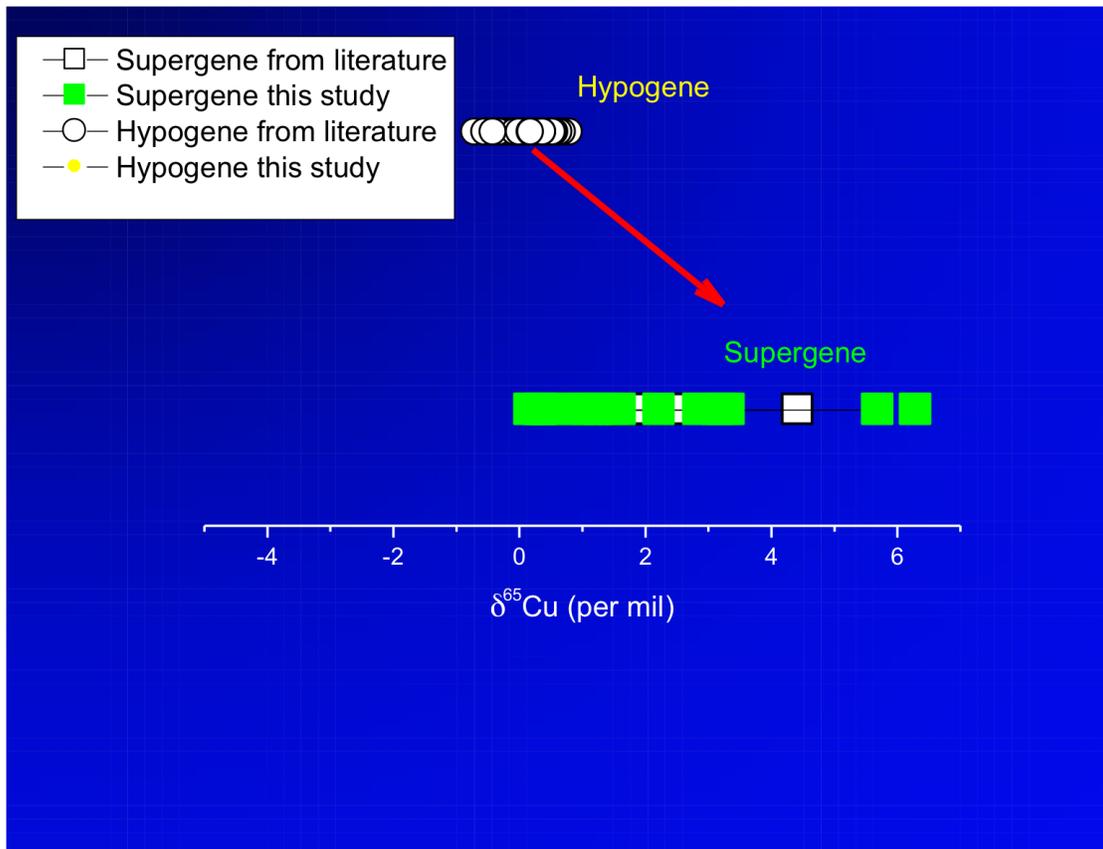


Figure 5

Figure 5 shows variations from that isotopic ratio. Another type of fractionation occurs in the hypogene or the high temperature mineralization. The standard that we use looks the same as high temperature mineralization. So there hasn't been much fractionation. If you look at the low temperature mineralization, there's been high variation, at least in these shown in the ratio in Figure 5. We're not talking about tons and tons and tons; it's about a variation in the third decimal point of the ratio. So it's not a giant fractionation but a significant one that can now be detected given the technology we have.

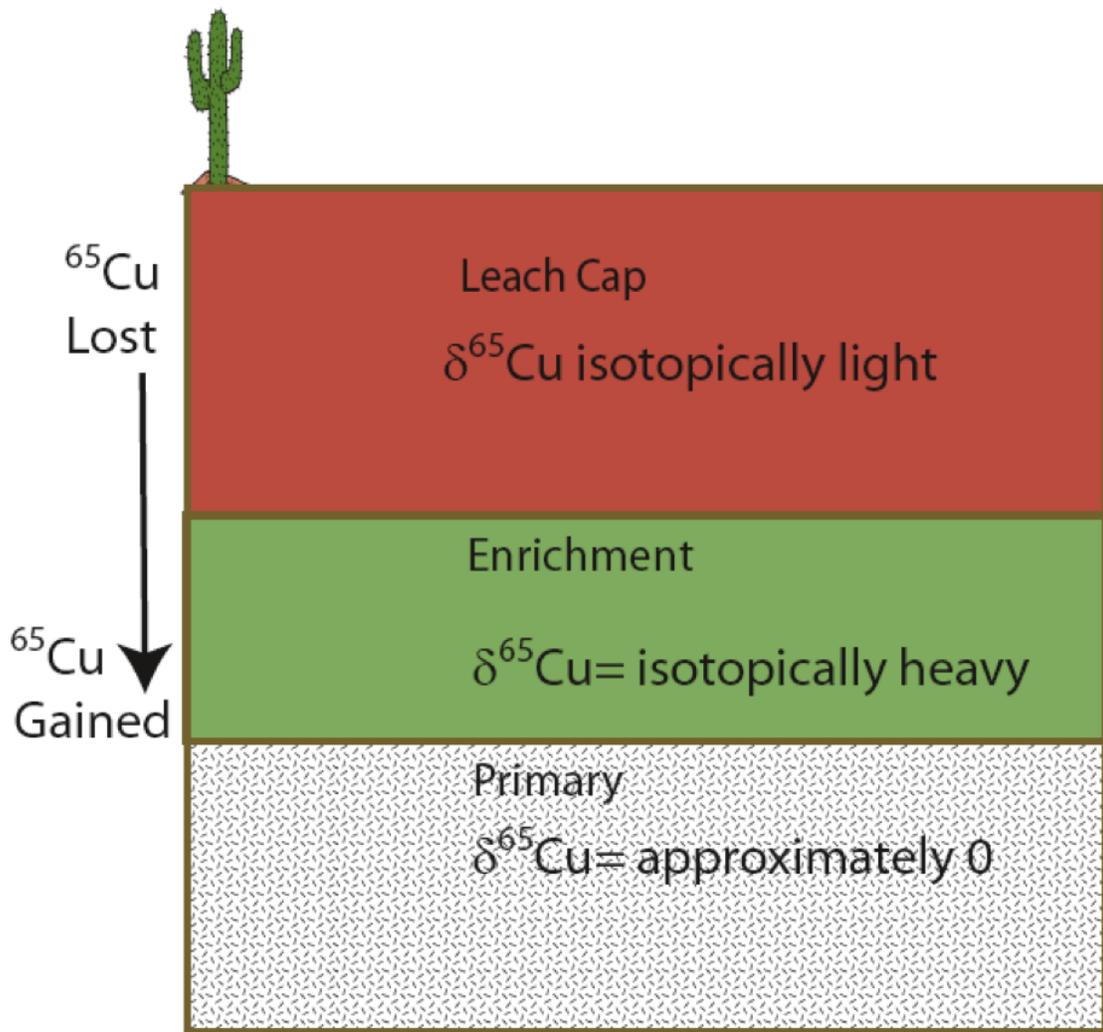


Figure 6: Cartoon Depiction of Process

Figure 6 shows the model that I developed to show isotope fractionation in these deposits. You can envision that all of the rock was center of the volcano. Then after everything was uplifted and weathered, when you leach the rock,  $^{65}\text{Cu}$ , which has a stronger bonding environment when it's oxidized, comes out of the leach cap or the copper minerals. Then when it's reprecipitated, the  $^{65}$  comes out of the solution in the enrichment zone. As a result, you get leach caps, which are in a sense isotopically light, and enrichment zones, which are heavier. The primary copper that I showed you before is around zero. We can use this pattern to compare and contrast different ore deposits.

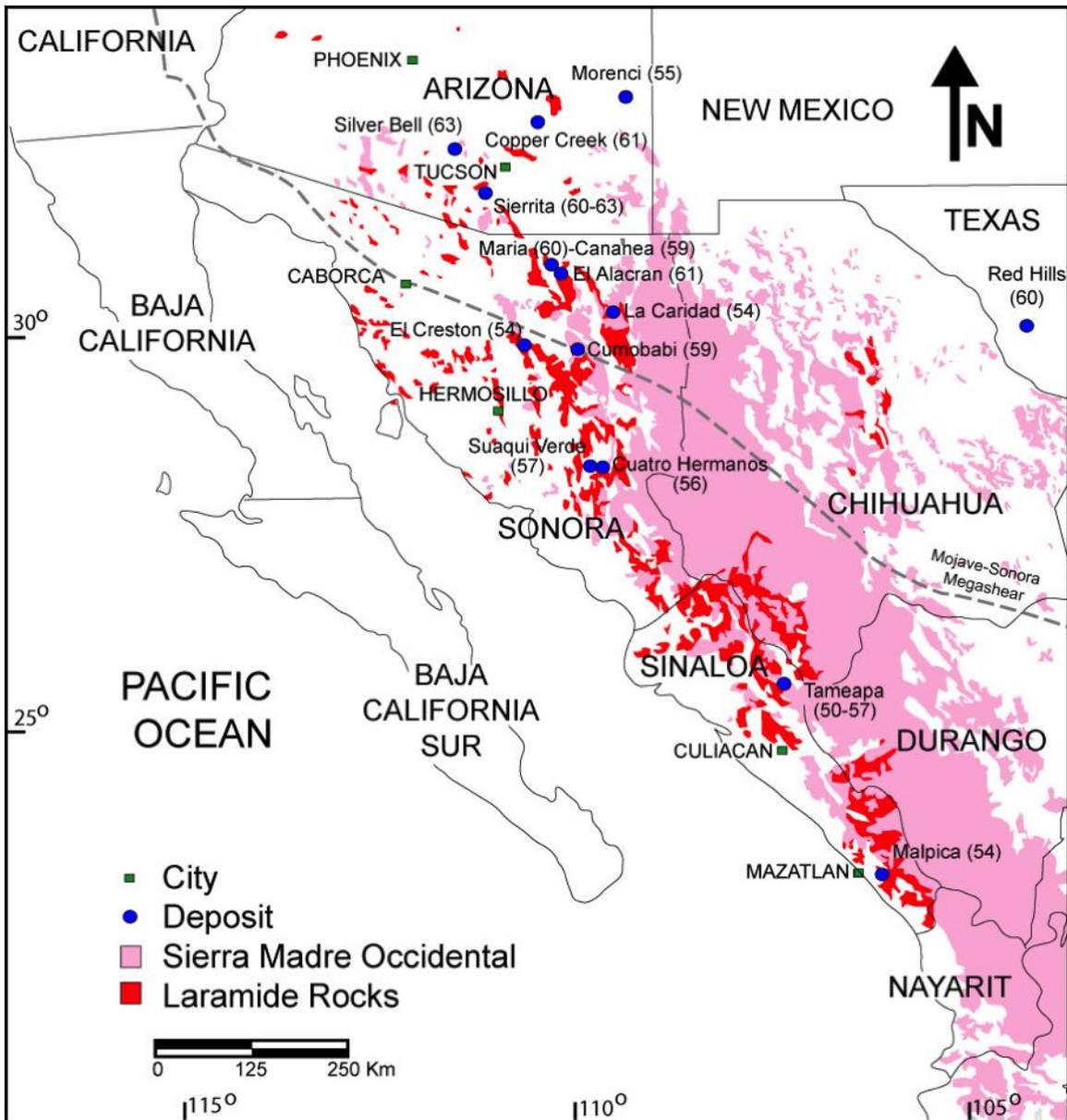


Figure 7: Example of Cu Isotope Fractionation in Southwestern PCD

I've applied this model in Southern Arizona. Tucson is the big green star at the top (Figure 7). I analyzed minerals in the Morenci, Silver Bell, and Ray Mines, always focusing on the leach cap and enrichment zones.

Figure 8 demonstrates that the predicted Cu isotope model exists at Silver Bell.

Mass Balance exists in Silver Bell, AZ

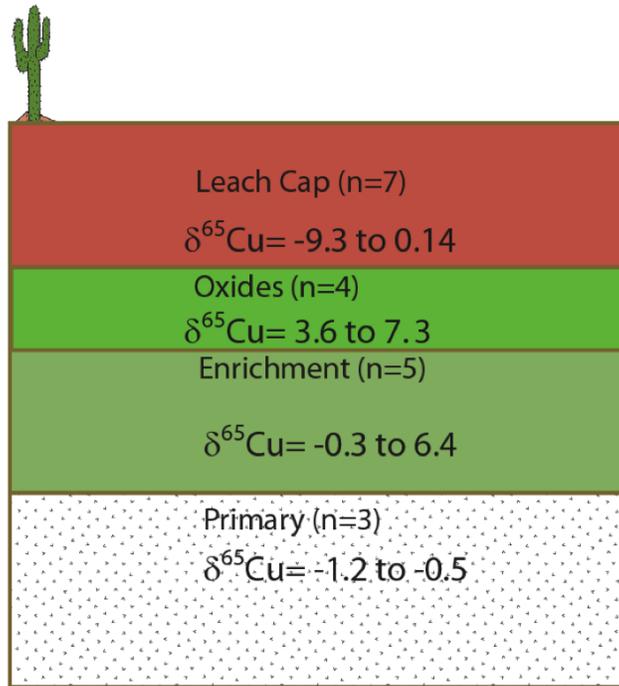


Figure 8: Development of Three Cu Isotope Reservoirs: An Example from Silver Bell, Arizona

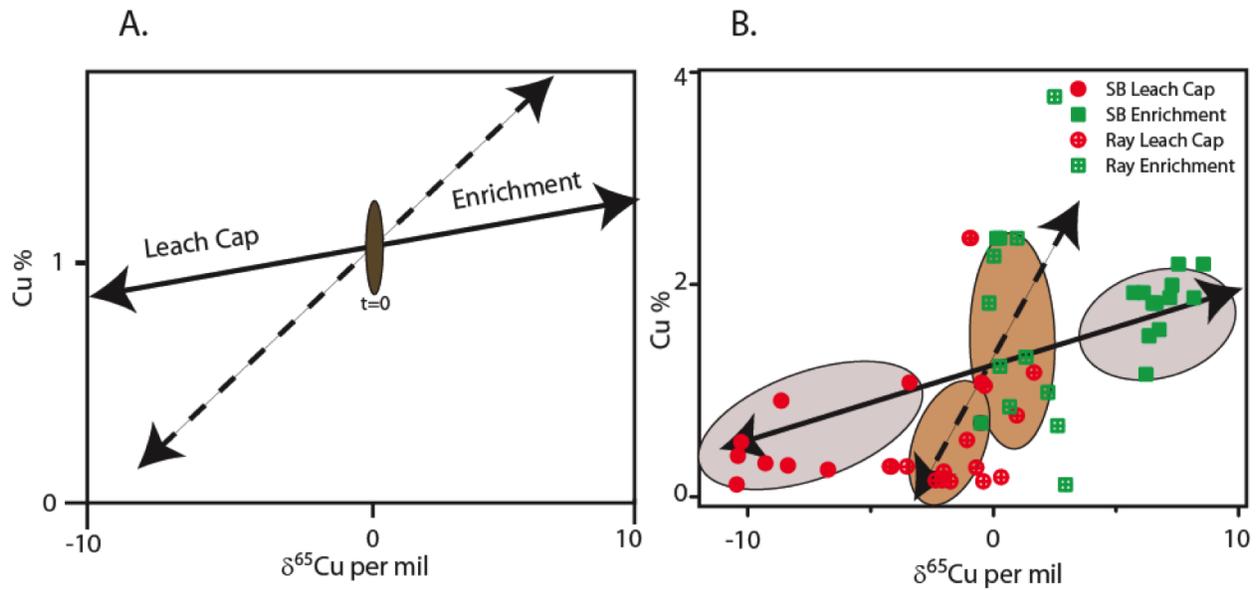


Figure 9: Comparing Silver Bell Data with Ray Data

Figure 9 shows two different models. The left shows a starting point for the copper isotope ratio and a copper percent. I have plotted here two different trajectories. The flat trajectory mimics data from Silver Bell Mine. The steep trajectory represents data from the Ray Mine.

On the right (Figure 9) grey ellipses represent Silver Bell and the brown ellipses represent Ray. In the comparison of these two data sets, you can see that there are distinct differences between Ray and Silver Bell. The data for Ray is not that separated. This suggests that there has not been much weathering at Ray. In contrast, in Silver Bell where we see a large fractionation of isotopes, it is likely that a higher degree of weathering occurred. An interpretation of these two occurrences is that when a greater degree of weathering exists, most of the copper leaks away and a large copper deposit does not form.

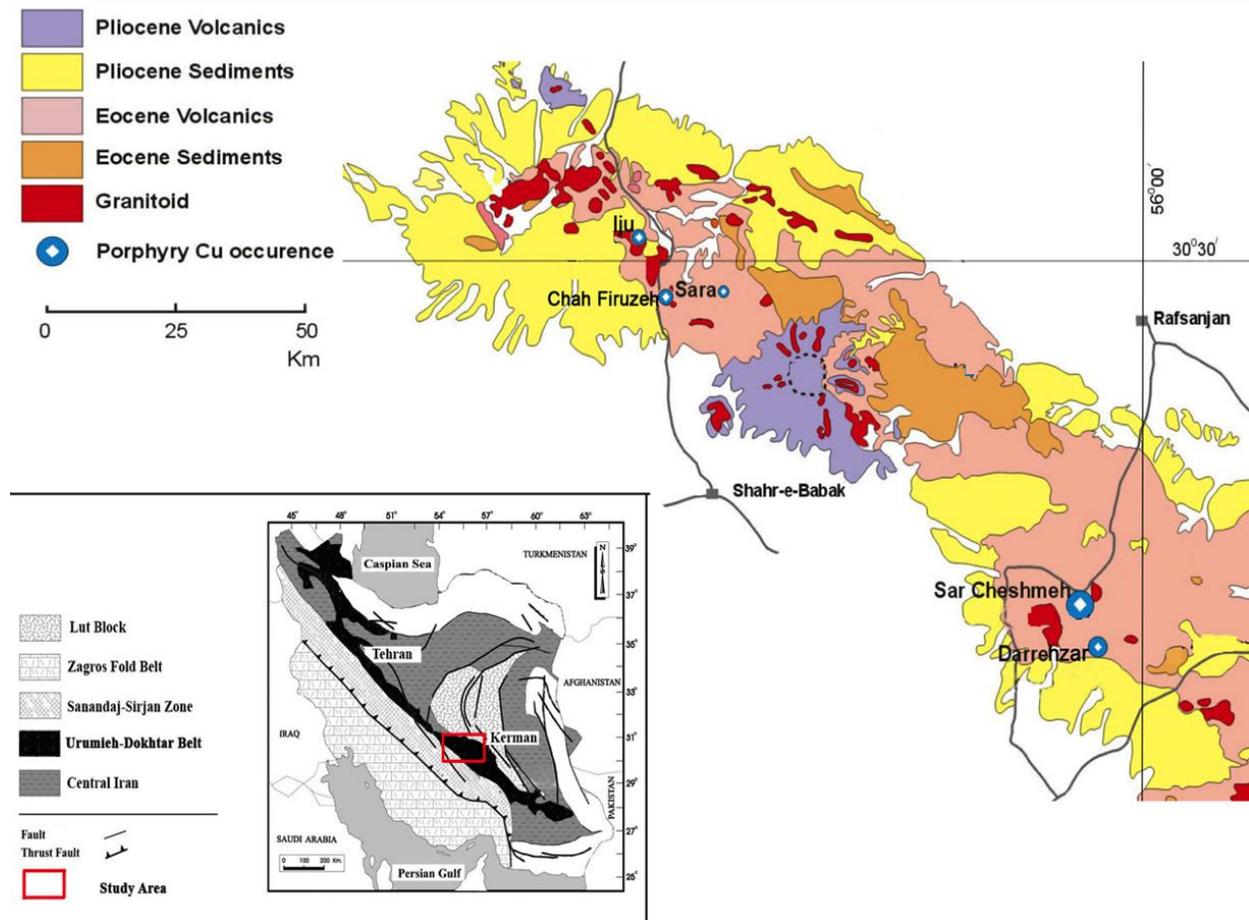


Figure 10: District Comparison of Cu Isotope Ratios of Leach Caps and Ores

I worked with four different deposits in Iran, looking at weathering (Figure 10). This is an ideal location to use copper isotope fractionation to explore for more copper deposits.

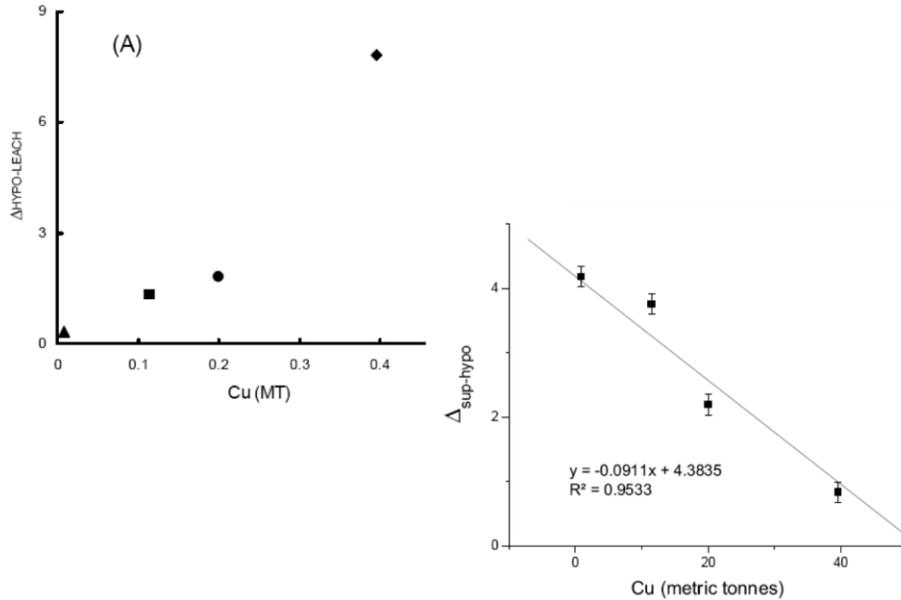


Figure 11: Relationship with Amount of Cu and Isotope Ratios

Analyzing samples from the leach cap and enrichment zones reveals a relationship between estimated sizes of the deposits and the copper isotope (Figure 11). On this diagram, you can see a variation in the isotope ratios that I look at and the total amount of copper that is present. You could use these once again in a predictive sense to choose new exploration areas.

To end the talk I want to describe an archeological application to my work. I used the isotopic composition of artifacts to fingerprint the origin of certain artifacts. People have been using metal isotope ratios in a variety of things to trace them since 1996. Within the first three years of such studies, two articles were published about people trying to look at metals and the isotope composition in metals to trace them to a specific source. None of the initial studies were very successful so nobody really started to do anything. I read the articles and I became interested, but did not act until I was in the laboratory measuring samples about two years ago.

When I'm running the instrument I'm always worried about contaminating my experiments. I don't want something to come into my solution that could destroy everything. One night I had change in my pocket and I thought, "Wow, I have pennies in my pocket and that's a ton of copper." Then I thought about how I handle acids all the time in the lab. So I thought that I could have had acids, in theory, on my finger when I just touched a penny and could have dissolved some of that copper and then it would destroy my experiment. Then I thought, "Wait, I can dissolve a penny. That's perfect." Pennies are a perfect experiment for copper isotopes.

I thought, at least when I first started doing this, is that we probably know where most of the copper comes in this country or where the United States purchased it. There probably should be some

pretty good records where we purchased copper to make a penny. I also thought that there would be variations in the pennies, so I measured them.

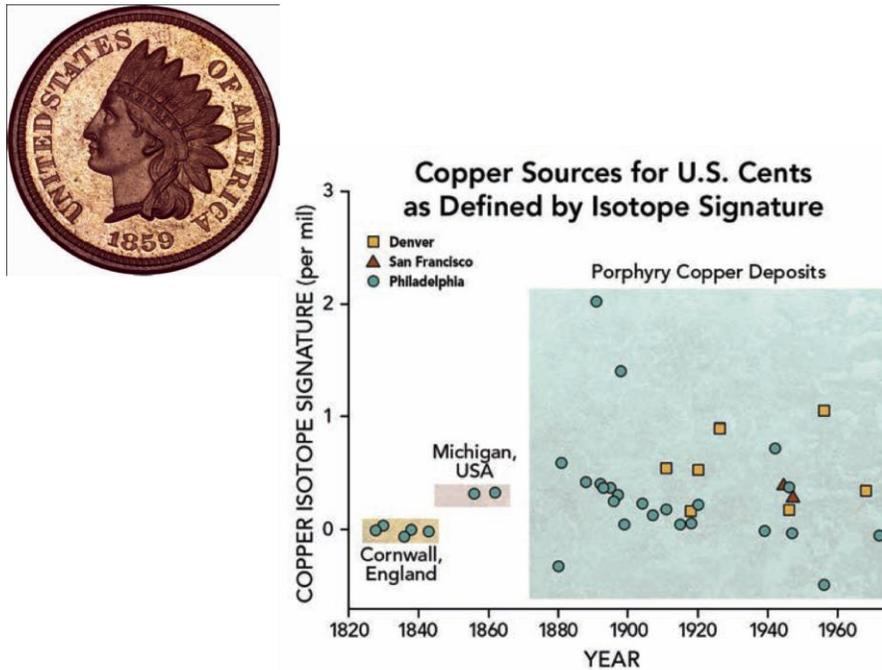


Figure 12

I collected about 60 pennies minted between 1900 to about 1960. The chart above shows copper isotope variations (Figure 12). I was excited to first note that there was variation.

Next I needed to target what to say about these variations. I talked to Dave Hsiung about how I could find out where the copper in the pennies came from. He suggested asking some people in Michigan because at some point the U.S. mint began using Michigan copper among other different sources to make pennies. After sending 342 emails (I saved every one of them), I found that no one had a clue.

I finally figured out that there is an official record of the Mint that the president of the Mint releases every year. I thought I would easily be able to access that document online. Wrong. I couldn't access it online, or find a hard copy here at Juniata. Penn State's library system didn't even have it. But the University of Arizona had every issue. I called my former student, Caitlan Zlatos ('05) who was a graduate student at the University of Arizona at the time and asked her to do me a favor. She examined all the records from about 1860 until about 1960 and found variations of where the U.S. Mint purchased copper. Since the Mint bought large amounts of copper from various places to use in any given year, the pennies would be a mixture of isotope ratios. The analysis would not point to one place.

I thought maybe if I went a little farther back in the historic record, I might be able to find a time when the Mint used a single copper source in the pennies. The problem is that when you go for coins

from years before 1880 on, the pennies cost hundreds of dollars. So it's not a penny anymore, it's a lot of money. When I bought 1860 pennies, they had little holes in them and they were destroyed but they still cost me about \$50. Then I bought coins minted between 1820 and 1840. They cost between \$150 to \$200 a piece. It's expensive to study pennies.

Unfortunately, records for coins before 1865 are not readily available to the public. In the records exist at the Mint in Philadelphia but I was told that I couldn't handle the documents myself, because I didn't have the credentials to do it. I needed to hire a historian to look at the specific years that I wanted to know where the copper came from.

The first thing I found was that the U.S. basically bought most of its copper from Cornwall until about 1840 and then around 1844, the United States actually found significantly large copper deposits in Michigan. Then from 1865 or so, then we purchased copper from a variety of different places. The next thing that I had to worry about was copper isotope information from Cornwall and then from Michigan. Luckily, since these are well-known areas, people had already looked at copper isotopes and had measured chalcopyrite and other minerals from Michigan. I didn't have to measure anything because the data was already published. When I looked at that the published numbers, they fit perfectly with what numbers I saw in the penny. That means if you're mining chalcopyrite out of a sole source, for instance Cornwall, the pennies made from the chalcopyrite retain the same copper isotope signature of the ore. This verifies that you can use the copper isotope signatures in artifacts and relate them to specific ore occurrences.

And it was basically 1830 – 1840, that many of these Cornwall mines started to go downhill in production. Most of these miners actually moved to the United States and then helped us mine out copper in Michigan and some other areas. So, it's quite interesting here because we were relying on England for everything, but then this period marks a gigantic gain in independence because no longer were we buying anything from Cornwall. We shifted to supporting ourselves. Not only does it show a social, historical, political thing but a difference in the ways and types of ores that we were able to extract out of the earth.

Other things that are neat when you look at the data, is that you can see variations that different mints of the same year, bought there are copper from different places. I think this is like 1954, where I have a line of 3 of these here from Denver, San Francisco and Philadelphia all basically got their copper from different places. I have overlapped in other years but it's just interesting to note these different signatures could be associated with different ore.

In summary, the isotopic approaches shown here demonstrate both their practical and academic applications.