Finding the Motherlode: Insights from Isotope Geochemistry

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INTRODUCTION

Volcanic eruptions are one of the most recognizable geologic phenomena and they draw extraordinarily large amounts of public interest. Most people recognize the importance of studying these types of mountains because volcanic activity can have a direct impact on everyday life. Geologists study various hazard-related aspects inherent with people coexisting near volcanically active terrains. We strive to explain the paramount questions of how, why, where, and most importantly, when will these volcanoes erupt. Aside from our fascination or necessary concern for survival during volcanic activity, there are other essential economic issues related to understanding the mechanics of volcanoes.

In this discussion we will focus on the processes that occur in the inner portions or 'guts' of volcanoes because large concentrations of metals of economic interest, such as gold, iron, copper, molybdenum and silver, occur in these areas. Portions of the earth's crust that contain elevated concentrations of metals of economic importance are called ore deposits. The definition of an ore deposit is necessarily linked with the market demand of a metal. Ore deposits can form in various geologic environments, and we will

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only talk about porphyry copper deposits that form in the inner portions of large stratavolcanoes found in continental arc settings. In this case, copper (Cu) is the dominant element of economic interest and the term porphyry describes the texture of the rock in which the deposits occur (containing both coarse/visible mineral grains that "swim" in a fine-grained groundmass of minerals).

While thinking about the plumbing systems of volcanoes, geologists are faced with describing the processes related to the creation of magma at great depths, percolation of magma through the crust, ponding of magma at shallow levels of the crust (<5 km) and finally to the exhumation and erosion of the stratavolcano. To develop an understanding of porphyry copper deposits we must study various branches of geology ranging from petrology and geophysics to geochemistry and hydrogeology because the genesis of these deposits involves high temperature interactions between the magma and the crust, and the low temperature reactions of the solidified crust with groundwater.

The processes that occur during the formation of these deposits are multiple and intertwined. Ultimately, geologists must integrate these various types of information in order to find a productive (meaning large concentration of metal that can be mined) porphyry copper deposit. In the following discussion, I will illuminate several geochemical tools and materials that geologists can use to assist in discovering productive porphyry copper deposits.

MODELS FOR PORPHYRY COPPER DEPOSITS

Porphyry copper deposits, which are major geochemical irregularities of the earth's crust, are characterized by anomalous concentrations of chalcophile elements (elements which commonly occur in sulfide minerals). These deposits are technically described as "large, low grade (about 1% contained copper) copper deposits" that commonly occur in association with felsic (siliceous, feldspar-rich) igneous rocks.[1] They are extremely important resources for copper and other metals such as gold (Au) and molybdenum (Mo). In fact, over 60% of all copper extracted from the earth is derived from these deposits and they are also the largest producer of gold.

Porphyry copper deposits are found in subduction zone environments, tectonic plate boundaries on the earth where oceanic crust (made of heavy ferromagnesium minerals) dives down or sinks underneath continental crust (containing lighter lithophile minerals, Figure 1).

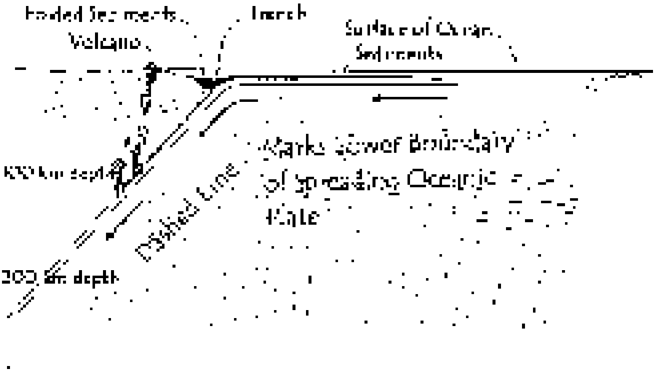

Figure 1- Cross section of the earth at a subduction zone.[2]

Most porphyry copper deposits are relatively young in comparison to the age of the earth because these deposits occur in large mountain ranges which experience intense erosion through time. For instance, more than 70% of porphyry copper deposits formed within the last 400 million years, which is young in comparison to the 4.5 billion year age of the earth.

The magmas associated with these deposits occur because of the intrusion of subduction-related magmas at shallow levels of the crust. In subduction zone environments, melt is generated due to the addition of fluids from the oceanic crust. The addition of fluid at this depth (~150 km) is thought to depress the melting temperature of the mantle, thus melt is created. Melt generated in the wedge portion between the lower continental crust and the subducting slab rises through the lower continental crust into the upper continental crust. The magma cools in the shallow portions of the crust (<5 km) and during this process the magma concentrates or 'exsolves' a fluid-rich phase that is less dense than the surrounding magma and ponds at the top of the magma chamber. Once the fluid pressure that accumulates at the top of the magma chamber exceeds the surrounding lithostatic pressure, the surrounding wall rock shatters and the fluids inject into the surrounding region and deposit metal-rich minerals. The subsequent development of large hydrothermal systems around these intrusions results in deposition of Cu-bearing minerals in thin veinlet fractures (centimeter cracks in the rock which are filled with minerals) termed ‘stockwork’. After volcanic activity ceases the volcanic edifice begins to erode and through time erosion denudes the mountain of volcanic rock to expose the ‘guts’ of the volcano. Groundwater interacts with the metal-rich sulfide minerals in the highly fractured wall rock. This interaction produces a dilute sulfuric acid, which serves as a mechanism to redistribute and further concentrate metals.

There are many theories on the reason why these deposits form.[3] The possible controls for mineralization include regional structures, a specific chemical and/or physical evolution of the magmatic and/or hydrothermal system, number of mineralizing events in an area, depth of erosion and the sources and availability of sulfur and/or the ore-forming metals. Geologists must consider all of these factors when evaluating potentially productive areas in the earth’s crust. In order to address some of these concerns we analyzed trace elements in the metal-bearing minerals to ascertain the source of the ore-forming elements and the timing of mineralization.

GEOCHEMICAL TOOLS

We used two types of isotope systems to assist in understanding porphyry copper genesis. The bulk of the work described below uses the radiogenic isotope system of rhenium (Re) and osmium (Os), and a small portion of the document describes our work with stable copper isotopes.

Establishing a relative sequence of geologic events is essential in understanding the genesis of porphyry copper deposits. Typically, the geologic history in these areas is extremely complex due to the intrusion of multiple magmas in one area coupled with the metamorphism of the surrounding wall rocks. As a starting point, basic field observations of cross cutting relationships are used to roughly clarify a simple chronology of an area. In order to further elucidate timing relationships, geologists use the natural radioactive decay of elements in minerals to quantify chronologies (one can measure the amount of parent and daughter isotope in a mineral and, by knowing the radioactive decay constant of elements, derive an age for the mineral). This is important in a regional geologic sense because the timing of porphyry copper deposits in an area appears to be constrained to spatial and age intervals in the geologic past.[4] Another aspect of these deposits is that they may represent multiple mineralization events. So, if an exploration geologist looking for the 'motherlode' finds several different mineralization events that cluster into a known interval of porphyry copper genesis, the probability that the prospect is an ore deposit increases.

Aside from chronologic information, geochemical data can provide information about the source of an element. By source, we mean the process whereby the mantle, crust or some mixture of the two melted and produced the magma and its associated minerals which contains the element(s) of interest. Identification of the source may provide insight as to why certain places in the crust contain deposits and other areas in similar geologic settings have no deposits. Source may also be related to the quantity of metals found in certain deposits. For example, if the mantle contains more copper than the crust then a melt with more of a mantle component may have more copper than one with a significant crustal component.

The isochron method is the conventional way to obtain source and geochronologic information.[5] In our study, analysis of Re-Os isotopes in ore minerals provided this essential timing and genetic information. The advantage of using this system is that this information can be obtained from the ore rather than from associated alteration minerals because Re and Os concentrate in sulfide minerals. The source of Os can be used to distinguish crustal and mantle reservoirs involved in ore formation because Re is more incompatible than Os during mantle melting. Crustal materials therefore have larger Re/Os ratios, and develop a higher ^{187}Os/^{188}Os isotope ratio with time compared to the mantle because ^{187}Re decays to ^{187}Os with a half-life of about 42 Ga (1 *Giga annum* = 1 billion years). The ^{187}Os/^{188}Os ratio in the current chondritic mantle is approximately 0.13.[6] Initial Os ratios greater than this can indicate a crustal source for Os and, by inference, other ore forming metals.

In this study we use the source of Os in oxides and sulfides as a proxy for the source of base metals. Initial Os ratios greater than the mantle serve as indication of a crustal source for Os and, by inference, other ore forming metals. Due to their siderophile and chalcophile nature, Re and Os are assumed to behave like other base and noble metals. The geologists Xiong and Wood provide experimental and theoretical evidence that documents a similar behavior of platinum group elements (PGE) in porphyry copper environments.[7] Though there is no direct evidence for an identical behavior of the PGE and base metals in porphyry copper systems, experimental data suggest the affinity of all metals for sulfur rich melts in magmatic systems.

The timing of mineralization can be more accurate in molybdenite because it contains orders of magnitude more Re than the common sulfides and effectively no initial radiogenic ^{187}Os. Therefore, it can be used as a high-precision geochronometer.[8]

CHRONOLOGIES

There are many examples of how Re-Os can be used to determine chronologies in different ore deposits. We recently conducted a study of sulfide minerals, alteration silicate minerals and minerals from surrounding intrusive rocks from the El Teniente copper deposits in Chile. The questions that the study addressed are how many mineralization events occurred and what intrusive event is responsible for the mineralization? Answers to these questions may provide insight into why these deposits occur in some areas and not in others.

El Teniente is the youngest PCD in the Chilean Andes and is the largest intrusion-related Cu-Mo orebody in the world, containing more than 75 metric tons (1 Mt = 1,000 kilos) Cu in hypogene ores exceeding 0.65% Cu and more than 1.4 Mt Mo in ores exceeding 0.019% Mo. Approximately 80% of the Cu and Mo at El Teniente occur within a stockwork of mineralized veins and hydrothermal breccias within biotitized basalts, diabases, andesites and gabbros in Upper Miocene country rocks. With the myriad of volcanic rocks that occur in the area, there are several possible sources for mineralization that range from older mafic rocks (which have more iron and magnesium minerals such as gabbros and basalts) to younger felsic rocks (which contain lighter lithophile elements and include andesites and 'granites').

The results of the study indicate that there were at least four distinct mineralization events that occurred over an interval of 2.5 Ma in this small portion of the crust (1 *Mega annum* = 1 million years). This evidence indicates that the genesis of the El Teniente ore deposit involved multiple copper rich magmatic events that occurred in the same area over a relatively long interval of time. Simply put, our findings support the notion of 'more is always better' with regard to mineralization events for generating super giant copper deposits in the earth's crust.

RE-OS SOURCE INFORMATION

We can use the Os ratios derived from isochron diagrams to ascertain the source of Os and use this approximation for the source of other ore forming elements (like gold, copper, iron). We used this method to conduct a regional study on porphyry copper deposits in the Andes and a detailed study of an ore deposit in Irian Jaya.

In the regional study on the Andean porphyry copper deposits, we have found some very interesting results which are summarized below. Typical concentrations for Os in both pyrite and chalcopyrite are between 7 and 30 parts per trillion (10^{-12} grams per gram), and between 0.200 to 10 parts per billion (10^{-9} grams per gram) for Re. It is important to note that the chemistry involved in separating Re and Os at the part per trillion (femtogram) level from sulfide samples is time consuming and extremely labor intensive. Lab analyses can cost on the average of $1000 per sample because the technique is so cumbersome. It is commonplace that several runs of the same sample are needed for valid results.

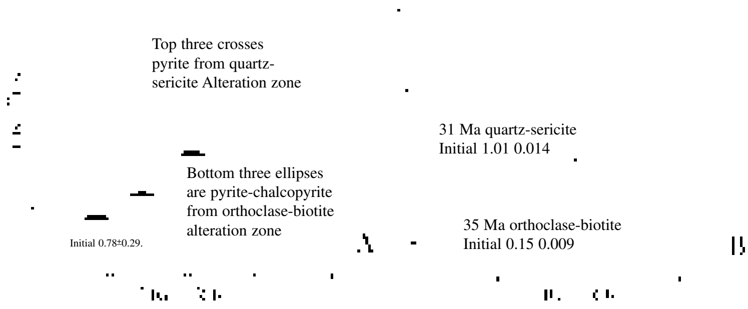

Figure 2- Examples of Re-Os data from Chilean ore deposits.

Re-Os isochrons from sulfides from these deposits yield ages, and initial ^{187}Os/^{188}Os ratios (Figure 2). The isotopic data reflect the relative contributions of copper from the mantle and crust in Chilean porphyry copper deposits. Nine ore deposits that reside in different tectonic terranes (distinct fault blocked portions of crust) and represent distinct epochs of mineralization (Figure 3) were studied.

Figure 3- Location map for the Chilean porphyry copper deposits and their ages of mineralization.

The initial osmium ratios of the sulfides taken from the highest temperature mineralization event at each of the deposits range from 0.15 to 5. These values are more radiogenic than the present chondritic mantle (~0.13), and indicate significant crustal contributions of Os to the magmatic/hydrothermal systems (Figure 4). There is a strong correspondence between the total copper content and initial Os isotopic ratios in base-metal porphyry deposits. The larger deposits have lower initial Os ratios than the smaller, less significant deposits. This relationship implies that larger deposits acquire a greater proportion of Os from the mantle. The initial Os ratio of samples in the central segment of porphyry copper deposits of northern Chile also decreases with decreasing age of the deposit. A plausible interpretation of the Re-Os data is that the later and larger deposits use regional tectonic and structural features that allow sampling of deeper, more primitive magmatic sources. These observations are not meant to represent ‘silver bullets’ for finding the motherlode, but can be viewed as additional weapons in the arsenal of tools used to decipher the genesis of these copper deposits.

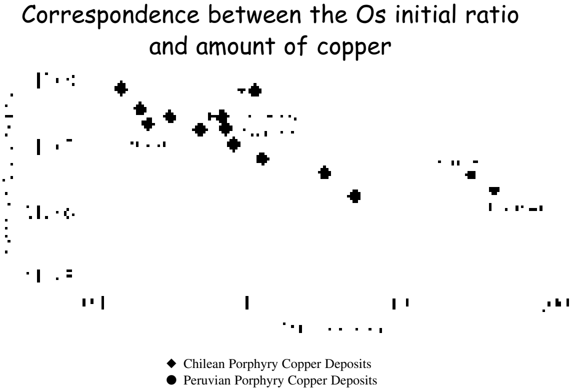

Figure 4- Relationship between Os initial ratio and copper present in various Andean ore deposits.

In Irian Jaya, we looked at the Grasberg deposit. Grasberg is the largest known porphyry Cu-Au deposit on earth containing about 2.1 billion tons of Cu ore at 1.2% Cu and 1.2 grams per ton Au. The ore deposit formed during recent magmatic events associated with the collision of the Australian and Indo-Pacific plates. The deposit occurs within the central mobile fold belt. In general, the magmatic rocks of this ore deposit intruded highly deformed/metamorphosed Proterozoic and Paleozoic through Cenozoic sedimentary rocks. The major issue we were concerned with in this study is if the surrounding wall rocks could be a possible source for the copper or gold found at this deposit. We discovered that the Re-Os isotope data indicate different crustal sources for the ore-forming elements at the Grasberg Cu-Au deposit and support a model in which gold is derived from sedimentary protoliths (wall rocks). The gold derived from these sources is concentrated by magmatic/hydrothermal systems. We have studied the surrounding sedimentary rocks and have found that the Os ratios present in the sedimentary rocks are similar to those found in the ores. This isotopic similarity quantifies the existence of a sedimentary source for gold in hydrothermal gold deposits. Economic geologists have pondered this question for decades and this study provides strong support for the importance of the crust as a source for metals. Thus, for the exploration geologist interested in the motherlode, there may be certain gold rich areas in the crust that could house productive ore deposits.

COPPER ISOTOPES

The field of studying transition metal isotopes is relatively new. Copper isotope fractionation has received little attention thus far, and no systematic mechanism for the observed fractionations has been clearly identified. When geochemists talk about fractionation of isotopes this means that during some geologic process a mineral grain or a fluid favors one isotope over another during crystallization.

Fractionation is not a simple concept to grasp; a useful analogy is to envision the distribution of chips during a game of blackjack. Assume you take $40 into a casino while on a visit to Las Vegas. You sit down at a table and the dealer gives you three $10 green chips and two $5 red chips. The initial ratio of chips is three green to two red, or 3:2. A short time later you have six green and two red chips, for a ratio of 6:2. You have been lucky and have 'fractionated' your chips through gambling and increased from the initial ratio of green to red by a factor of two. This same 'unequal distribution' occurs in nature on the atomic level when minerals and fluid react or interact. For instance, imagine a fluid that has a ratio of three atoms of ^{65}Cu and two atoms of ^{63}Cu (3:2). If the mineral that precipitates from this solution has six ^{65}Cu to two ^{63}Cu (6:2), then the solid mineral is fractionated or enriched by a factor of two in comparison to the starting solution. Geologists strive to understand what causes fractionation so that when observed in natural samples they can infer what must have happened to produce this ratio in nature. The causes are certainly more complex than luck as demonstrated in the gambling analogy.

When envisioning atomic scale interactions, factors that influence fractionation could include varying temperature, crystal structure, the redox potential of the atoms in the sample and the basic chemistry of the solutions involved. This is a relatively new field in geochemistry, and the relevance of exploring how and why these isotopes fractionate will have a direct impact on the future use of copper isotopes in fields ranging from exploration economic geology to tracing biologic activity.

The first exploratory study of Cu isotope fractionation by measuring Cu isotope ratios in ores derived from low temperature mineralizing fluids. Since then, few utilized Cu isotopes to address geologic problems because of imprecise instrumentation. However, during the past six years there have been technological advances in mass spectrometers that allow for the precise and accurate measurements of transition metal isotopes.

We designed experiments to help us gain a basic understanding of what causes copper isotopes to fractionate. Once this is understood we can explain some of the natural variation that has already been found in minerals from porphyry copper deposits. In order to accomplish these goals, we examined the fluids and solids at different intervals during the leaching of chalcocite in acidic solutions over a long period. We chose this mineral because:

1. It is the most common copper mineral used to extract copper from ore deposits.
2. During dissolution of chalcocite there are several other minerals that precipitate out of solution, so we were able to see if different crystal structures favored one copper isotope over another during dissolution and precipitation.
3. It is known that certain bacteria aid in the dissolution of chalcocite, therefore, we added these bacteria to the experiments to see what influence they may have during the leaching process.

Figure 5 is a summary figure of our results. It illustrates that there is an extreme fractionation of copper isotopes during the dissolution of chalcocite over a one-hundred-day period. Note that the starting copper isotopic composition of the chalcocite is the thick black line and the solutions are the data points of the fluid as measured throughout the leach period. It is important to note that higher copper isotope values indicate that the heavier isotope (^{65}Cu) was favored during the formation of the mineral and negative values indicate that the lighter isotope (^{63}Cu) was favored during the formation of the mineral. One can see that the solutions become enriched in the heavier Cu isotope during the leaching process. We analyzed the various mineral phases present during the dissolution and can link crystallographic changes to the observed isotopic changes seen in solution. The relevance of this study is that we found a cause (crystal structure) for an observed copper isotope fractionation. Tied in with this work was a smaller study on the influence of bacteria on the fractionation process. In these experiments, we observed that the bacteria used in the leach also favor the heavy isotope during dissolution. This is important because we can demonstrate that the ^{65}Cu is favored during biological reactions along with the crystallographic controls. Therefore we feel that there must be interplay among these variables that produce these observed fractionations. This is important because observing copper isotope fractionation in nature does not necessarily indicate the occurrence of one process (biological) over another (crystallographic/ kinetic).

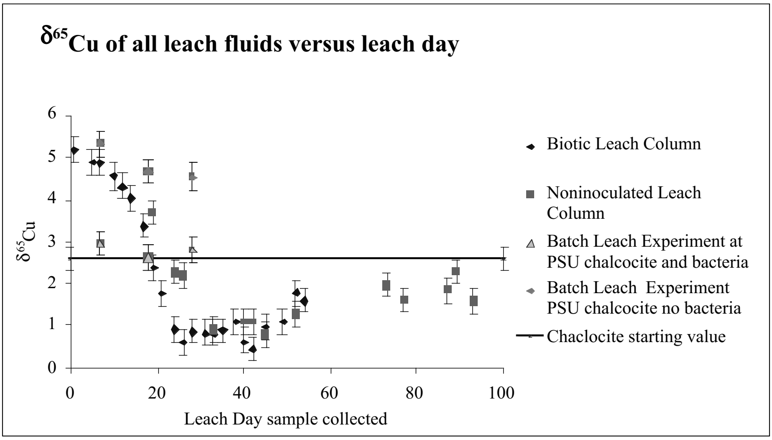

Figure 5- Copper isotope data collected from the leach pad.

CONCLUSIONS

This brief review summarizes the directions that my research has taken over the past three years. We continue to explore relationships in copper, and Re-Os isotopes. Our aim is to integrate the academic goals of describing how the earth works and industrial goals of finding feasible resources. To this point, we can qualitatively state that:

1. Re-Os radiogenic isotope results indicate multiple events that have mantle sources and can produce a ‘motherlode.’
2. Transition metal stable isotopes may indicate a relative duration of secondary leaching and the importance of biologic agents during the process.

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NOTES

[1] J. M. Guilbert and C. F. Park, *The Geology of Ore Deposits* (New York: W. H. Freeman, 1986), p. 985.

[2] See www.usgs.gov.

[3] A. H. Clark, "Are Outsize Porphyry Copper Deposits Either Anatomically or Environmentally Distinctive?," In B. H. Whiting, C/J. Hodgson, and R. Mason eds., *Giant Ore Deposits* (Society of Economic Geologists, Special Publication 2, 1993), pp. 213-283.

[4] T. E. McCandless and J. Ruiz, "Rhenium-Osmium Evidence for Regionally-timed Mineralization Events in Southwestern North America," *Science,* 261, (1993), p. 1282.

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[6] R. J. Walker, R. W Carlson, S. B. Shirey, and F. R. Boyd, "Os, Sr, Nd, and Pb Isotope Systematics of Southern Africa Peridotite Xenoliths; Implication for the Chemical Evolution of Subcontinental Mantle," *Geochimica et Cosmochimica Acta,* 53 (1989): p. 1583.

[7] Y. Xiong and S. Wood, "Experimental Quantification of Hydrothermal Solubility of Platinum-group Elements with Special Reference to Porphyry Copper Environments," *Mineralogy and Petrology,* 68 (2000), p. 1.

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