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RE-OS ISOTOPES OF BASE METAL PORPHYRY DEPOSITS

By
Ryan Dilip Mathur

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF GEOSCIENCES
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Ryan Dilip Nathur entitled Re-Os Isotopes of Base-Metal Porphyry Deposits and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

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SIGNED
Acknowledgements:

There are many people that have provided help and guidance throughout this study. I would first like to thank my wife and family for their support. Joaquin Ruiz has made my experience here wonderful. His enthusiasm for the variety of projects, assistance in preparing the articles and most importantly financial support are greatly appreciated. I would also like to thank Spencer Titeley for spending enormous amounts of time and energy teaching and discussing multiple topics in ore deposits with me. Another very important figure in this study is Francisco Munizaga, his organization of field trips, thousands of emails and constant supply of well-constrained samples made the projects possible.

Extracting trace quantities of Re-Os out of sulfide minerals is extremely difficult, the chemistry and analysis is cumbersome. I would like to thank Mark Baker, Claire Freydier, John Chesley, David Steinke, and Tom McCandless for their suggestions and direction in lab. The thesis was also greatly aided by interactions with fellow students. The conversations with and samples provided by Stacie Gibbins, Ruben Padilla, Richard Thompson, and Patrick Herb are valued.

I appreciate the thoughtful comments and thorough reviews of this thesis by my committee members: Jonathan Patchett, Bob Downs, and George Zandt. I acknowledge the critical comments of the thesis by Mark Barton.

Many thanks are in order for Chris Eastoe, Gerry Ray, Marcos Zentilli, Fernando Tornos, Robert Marschik, John-Mark Staude and BHP, Rich Leville and Phelps Dodge for their financial aid, supply of samples, and engaging conversations about these topics.

I would finally like to thank Jo Ann Overs, Susan Huatala, and Erika Weitzel for helping find Joaquin. That has been one of the most challenging tasks in completing the thesis!
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Abstract
This study uses Re-Os isotopes from sulfide minerals (molybdenite, pyrite, chalcopyrite, bornite, sphalerite, arsenopyrite, and galena) and magnetite from high (400-500°C) and low (<300°C) temperature mineralization assemblages associated with the intrusion of igneous rocks to trace the source of Os and by inference the other metals. The source of Os is used as a proxy for the source of copper and gold in these systems. Concentrations of Re-Os for all sulfides except molybdenite in various deposit types vary from 0.005-2 ppb Os and 0.120-500 ppb Re. Initial $^{187}\text{Os}/^{188}\text{Os}$ ratios derived from isochron plots ranges from 0.15-50. These data show interesting relationships among deposits of different styles within the district, region, and worldwide scales.

On the district-deposit scale, Re-Os isotopes illustrate a complex behavior for the source of Os and by inference other transition and noble metals. The source of Os can be linked to one intrusive event, multiple intrusive events, and the sedimentary rocks into which the magmas intersect.

On a regional scale, in the Andean Cordillera, Re-Os isotopes reveal a correspondence between the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio from sulfides of the ore deposit and amount of copper present in porphyry copper deposits. Eleven deposits sampled from different crustal blocks and different mineralization ages form a trend in which deposits that contain large amounts of copper have less radiogenic $^{187}\text{Os}/^{188}\text{Os}$ initial ratios, suggesting a greater mantle component. Smaller deposits have more radiogenic Os suggesting greater crustal components.

On a global scale, the significant observation for the deposits that form in arc environments is that all of the calculated initial $^{187}\text{Os}/^{188}\text{Os}$ ratios are greater then the
chondritic mantle. This indicates that there must be a crustal source (recycled in a metasomatized mantle, lower/upper continental crust, or subducting slab) that contributes Os and by inference other metals present in porphyry coppers. Another feature of the data set is that gold-bearing systems in arc environments associated with porphyry intrusions have crustal signatures (0.5-2.5) regardless of the style of the related ore body. For instance, the low/high sulfidation epithermal gold systems in Bucaramanga Columbia (\(^{187}\text{Os}/^{188}\text{Os} \text{ initial 1.2}\)), the massive sulfide ores of the Grasberg, Irian Jaya (\(^{187}\text{Os}/^{188}\text{Os} \text{ initial 0.7-1.2}\)), and Cu-Au skarns in the Hedley District, British Columbia (\(^{187}\text{Os}/^{188}\text{Os} \text{ initial 1.7-2.5}\)) all have large crustal components.
Chapter 1 - Introduction to the Present Study

Introduction

The objective of this study is to use Re-Os isotopes to address fundamental issues concerning the metallogensis of porphyry base-metal deposits. The two main pieces of data obtained from Re-Os isotopes in sulfide and oxide ore minerals are the source of the Os (and by inference the other metals) and timing of mineralization. This data can provide relevant information regarding ore genesis models. Important questions concerning ore genesis in arc environments include:

1. Are metals inherent to the intruding magma associated with mineralization or are metals acquired from the surrounding host rocks?
   a. A related question is, do specific terranes imprint metal sources in ore deposits?

2. Most ore deposits have multiple intrusive events, do the source of the ores reflect various pulses of magmatism or is the mineralization simply associated with one intrusion?

3. Is there one source for all of the metals (Cu, Au, Zn Pb....) associated with one intrusion, or are there distinct sources for certain metals?

4. Porphyry copper deposits normally occur in clusters in time and space. Does the source of metals in certain districts reflect regional processes responsible for this type of distribution?

5. Are there differences for the source of metals between ore deposits that form in island arc versus continental arc settings?
6. Can Re-Os systematics be used to characterize or even categorize differences between various ore styles associated with arc magmatism?

These are general issues in which quantitative evidence is lacking or not conclusive. In order to address these comprehensive questions concerning porphyry metallogenesis, this study presents results of a variety of ore styles found in different porphyry environments such as porphyry copper deposits, epithermal gold deposits, copper-gold skarns, and iron oxide rich Cu-Au mineralization. Due to the various perspectives presented in the following documents this work can generally be seen on three levels, the deposit, the region, and global scale.

Figure 1.1 presents a simple hypothetical cross section of the types of mineralization associated with convergent margin magmatism. All of the previously mentioned styles of mineralization are schematically related to an intrusive event. Differences in classification of these styles are based on the dominant economic elements of interest and the silicate alteration that is coupled with mineralization. We chose prominent mineralization events of each style found in different parts of the world.

Porphyry copper deposits are perhaps the most recognized style of mineralization in convergent margins. These deposits are defined as large, low-grade ore bodies that are centered about an igneous source (Pierce and Bolm, 1995; Sillitoe, 1988; Guilbert and Park, 1986; Tittley, 1982; Gustafson and Hunt, 1975). Plutonic rocks normally associated with copper mineralization range in composition from diorite to quartz monzonite. The deposits are characterized by a core of hypogene alteration (which includes the assemblages of biotite-orthoclase, and quartz-sericite) and mineralization with
chalcopyrite, bornite and sometimes molybdenite, as the minerals that host the economic elements of interest. Many geochemical studies of the ores and related rocks of these systems indicate metals are inherent to the intruding magma.

Skarns are part of the porphyry family. The only difference is a change in host rock alteration in which calcsilicates characterize the dominant alteration minerals. Another genetic class of ore deposits related to igneous rocks in arc environments is iron oxide rich copper-gold systems. These systems appear to be related to igneous rocks, however the exact process that dominated during their genesis is debated.

Sulfide and oxide samples were taken from high temperature hypogene alteration assemblages from ten porphyry copper deposits in Chile, three in Peru, one in British Columbia, two in the south Pacific, and one iron oxide deposit in Chile (Figure 1.2). Each suite of samples collected attempted to address the questions above. Appendix A provides information about sample locations and descriptions of all the phases analyzed, along with their associated silicate alteration minerals. The following chapters are organized in a way to describe the source of metals within an ore deposit (chapters 2 through 4), among a region of related ore deposits (chapter 5), and between different types of porphyry copper deposits (chapter 6 and Appendix E).

The second chapter (submitted to *Economic Geology*) of the thesis establishes genetic links between mineralization and the intrusion of intermediate rocks at Candelaria, Chile. This study quantifies genetic links between mineralization and associated magmatism by providing similar Os isotopic signatures of sulfide mineralization and magmatic magnetites. Chapter three (in *Earth and Planetary Sciences*...
vol. 183, 2000, p.7-14) focuses on the Grasberg copper-gold porphyry of Indonesia. These results illustrate distinct sources for gold-rich and gold-poor ores in the deposit. This study clearly illustrates that Os could be sourced from sedimentary rocks, as well as associated with the intrusion. Chapter four (accepted Mineralium Deposita) explores the relationship of epithermal gold mineralization to porphyry style mineralization. The epithermal gold deposits of Bucaramanga, Columbia demonstrate a crustal Os component for the ores present and an apparent difference between low and high sulfidation type epithermal systems.

The final two chapters cover regional and global observations concerning porphyry metallogenesis. Among the region of Andean porphyry copper ore deposits there is a relationship between the size of the ore body and the Os isotopic signature of the ores. Chapter five (in Geology vol.28, 2000, p 555-558) describes this relationship by highlighting its geologic and perhaps economic/exploration potential. The last chapter summarizes the previous chapters and compares Re-Os observations of all the deposits. This chapter incorporates reviews and perspectives from subsidiary analyses of low concentration sulfides. It concludes that there are multiple, crustal sources for copper-molybdenum deposits of Andean Cordillera and copper-gold deposits of the South Pacific and British Columbia. Re-Os contents of ores within these geographically and geologically distinct areas perhaps highlight differences between porphyries that occur in continental versus island arc settings.
Re-Os isotope systematics

The utility of Re-Os radiogenic isotopes applied to ore deposits is starting to be realized. Large uncertainties surrounding the half of $^{187}$Re and the lack of developing a dependable technique for measuring and extracting these elements from geologic materials initially inhibited its use. These procedural problems were overcome in the late 80's and early 90's with the advent of new techniques for extraction of these elements (Schoenberg, et al., 1999; Shirey and Walker, 1995; Creaser et al., 1991, McCandless and Ruiz, 1991; Volkering et al., 1991, Walczyk et al., 1991, Walker et al., 1989, a, b, 1986, Russ et al., 1987; Luck and Allegre, 1980; Luck et al., 1980; Naldrett, 1984). The results presented in this study were obtained by a distillation technique similar to Frei et al. 1998, with certain modifications to ensure the oxidation of Os in the sample. Due to the lack of studies analyzing low concentration sulfides (Freydier et al. 1996, Ruiz et al., 1997), the procedure used here is carefully reviewed in Appendix C.

$^{187}$Re decays to $^{187}$Os by beta emission, and it has a half-life of 42.3 Byr. (Smoliar et al., 1996; Lindler et al., 1989). The typical concentrations of these elements in a variety of rock types are plotted in Figure 1.3. These platinum group elements are categorized as chalcophile and slightly siderophile by Goldschmidt's classification. This general observation implies that Re and Os behave like elements of economic interest such as copper, lead, zinc, and other PGE elements. Re and Os therefore concentrate in sulfide phases (metal rich) rather then silicate minerals. The importance of this behavior in relationship to ore deposits is that chronologic and genetic information can be obtained from ore mineral rather than associated alteration silicates.
Re and Os are geochemically considered compatible elements, however, distribution coefficients (\(C_{\text{melt}}/C_{\text{solid}}\)) calculated for Re are orders of magnitude larger than for Os (Roy-Barman et al., 1996). This implies that during melting events Re will be enriched in the melt compared to the residual material. Thus, the melt will acquire a larger Re/Os ratio and evolve a greater \(^{187}\text{Os}\) isotopic signature (Fig. 4).

Evidence signifying the involvement of mantle and crustal domains during metallogenesis can be traced through the Os isotopic character of the ores in porphyry copper deposits. The source of Os that is revealed by the ores can be used as a proxy for the source of the economic elements of interest. Due to their siderophile and chalcophile nature, Re and Os are assumed to behave like other base and noble metals. Xiong and Wood (2000) and Wood (1987) provide experimental and theoretical evidence that documents a similar behavior of platinum group elements (PGE) in porphyry copper environments. No direct evidence illustrates an identical behavior of the PGE and base metals in porphyry copper environments, however experimental evidence illustrates the affinity of all metals to sulfur rich portions/ melts in magmatic systems (Sattari et al., 1998; Fleet et al. 1996; Peach et al., 1990; Stone et al., 1990; Mountain and Wood, 1988).

Isochron plots of the data were used to obtain timing and source information for the low concentration sulfides. Principles of isochron plots and associated statistical analysis is reviewed extensively in Faure 1986 and Dickin 1993. The general equation of a line on the diagram is defined as:

\[
\frac{^{187}\text{Os}}{^{188}\text{Os}_m} = \frac{^{187}\text{Os}}{^{188}\text{Os}_i} + \frac{^{187}\text{Re}}{^{188}\text{Os}} (e^{-\lambda t} - 1)
\]
where \( m \) = measured value, \( I \) = initial value, \( \lambda \) = decay constant, \( t \) = time. Earlier studies used \(^{186}\text{Os}\) for the denominator, however isobaric interference of \(^{186}\text{W}\) and the alpha decay of \(^{190}\text{Pt}\) to \(^{186}\text{Os}\) promoted the use of the more reproducible \(^{188}\text{Os}\) mass. The decay constant \( (\lambda) \) for \(^{187}\text{Re}\) used in this study is \( 1.66 \times 10^{-11} \) as calculated by Smolar et al. (1996). A key feature for treating the data in an isochron plot is error calculation. All of the data presented in the following paper account for the greatest possible deviation of isotopic ratios, which is caused by the variation of the Os blank. In depth discussion of the blank and its effect on the data are in chapter 5 and Appendix C.

Along with the chronologic information obtained from isochrons, some of the ore deposits presented have molybdenite ages. Molybdenite can be treated differently than the other lower concentration sulfides because molybdenite accommodates relatively no initial Os (Luck and Allegre, 1982). Re contents of molybdenites range up to a percent (Suzuki et al. 2000; Stein et al., 1998; McCandless et al., 1993), whereas the highest concentrations of Re in lower concentration sulfides is around 100 parts per billion. Therefore, molybdenite can be seen as an ideal geochronometer since only \(^{187}\text{Os}\) is produced by the decay of \(^{187}\text{Re}\). The time equation above can be reduced simply to:

\[
^{187}\text{Os}/^{188}\text{Os}_m = ^{187}\text{Re}/^{188}\text{Os} (e^{\lambda t} - 1)
\]

The large concentration of both elements in molybdenite allows for the calculation of mineralization ages with very low errors. In appendix B there is a presentation of Re-Os molybdenite ages that corroborate the age determinations from the isochrons derived from the low concentration samples of the deposits analyzed.
The reliability of the ages obtained from both isochrons and molybdenite rely on the ability of Re-Os to remain closed after deposition. Rigorous studies have proven that low temperature porphyry related fluids (Suzuki et al. 2000; McCandless et al. 1993) could easily alter molybdenites. Their studies suggest that all ages should be reproduced in order to ensure that calculated ages are a mineralization age not ages of subsequent alteration. Thus, the molybdenite ages are duplicated throughout the study. Also, we choose deposits that have had extensive geochronologic work preformed on the altered rocks determined by K-Ar, Ar-Ar, or U-Pb in order to support the Re-Os calculated ages. Most of the calculated molybdenites fall within the age ranges set by the other isotope systems.

In consideration of the low concentration samples, there have been several instances in which the Re-Os isotopic system appears to be open in certain samples regardless of the type of ore deposit. Mathur et al. (1999) presents an isochron for pyrite ores of the Iberian Pyrite Belt. Three results clearly lie on either side of the isochron and could indicate addition or subtraction of either element subsequent to deposition. Similar isotopic heterogeneity in massive sulfide ores associated with ancient Proterozoic oceanic crust was found by McCandless et al. (1998). Chesley (2000) presents Re-Os evidence from the Bingham, and Urad-Henderson Porphyry Copper deposits in which magnetites appear to retain genetic and timing information whereas the two sulfide results lie distinctly off of the magnetite isochron. Munizaga et al. (in preparation) documents a complex Re-Os isotope behavior in which no isochrons could be constructed for sulfides linked to Chilean manto deposits. Burton et al. (1999) also found Re-Os mobility
consequent to crystallization in rocks related to the ultramafic-mafic intrusions of the Lewisian Archean rocks of northwest Scotland. This evidence does not preclude the utility of Re-Os analysis of low concentration samples; rather it suggests the need for construction of isochrons with multiple analyses to ensure internal consistency of the Re-Os data sets.

In conjunction with isotopic closure of the Re-Os system, only one study has calculated, through experimental diffusion results, hypothetical closure temperatures for Re-Os in sulfide phases (Brenan et al. 2000). Their findings suggest that pyrrhotite has a closure temperatures similar to Ar in biotite which is around 350°C, whereas much higher closure temperatures are found for pyrite ± minor amount of chalcopyrite at about >500°C. This evidence led them to suggest that pyrrhotite could be recording later thermal events in mineralization, rather then the actual mineralization age. With regards to this study, the high closure temperature calculated for pyrite provides further evidence for the dependability of producing mineralization ages rather then alteration ages with Re-Os isochrons constructed by pyrite and chalcopyrite.

Goals of the Study

There are many important processes responsible for the genesis of porphyry copper deposits such as regional structure, specific hydrothermal systems, sources sulfur, volatility content of the magma, and sources of metal. In this contribution, we address the six questions outlined from the perspective of the source of metals. The strategy of this study is use isochron plots from low concentration samples to constrain initial $^{187}$Os/$^{188}$Os ratios, and obtain precise and accurate chronologic information from
molybdenites. Rigorous isochron plots of the data constrain initial ratios that confidently illustrate crustal and mantle signatures of Os and by inference the sources for metals in the deposits. Due to the large error associated with isochron plots from low concentration samples, molybdenite age calculations are used to pinpoint when mineralization occurred in the large range of alteration ages that usually overlap the error of the age on the low concentration isochron. With this approach, accurate Re-Os source and timing information from sulfide minerals provides essential data for the formulation of ore genesis models.

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Chapter 2- Re-Os molybdenite ages for mineralization and source information from low concentration sulfides for the iron oxide-rich Cu-Au ore at Candelaria, Chile

Abstract

Re-Os data from hydrothermal magnetite and sulfides from the Candelaria mine, Chile, and magmatic magnetite from spatially associated granitoids of the Copiapó Batholith were used to constrain genetic links between the iron oxide-rich Cu-Au mineralization and the batholithic intrusions in the area. Re-Os molybdenite ages of 114.2 ± 0.6 Ma and 115.2 ± 0.6 Ma from Candelaria constrain the age of mineralization. These ages coincide with previously reported 40Ar/39Ar biotite ages from Candelaria and Punta del Cobre district of 114.1 ± 0.7 Ma and 114.9 ± 1.0.

The initial $^{187}\text{Os}/^{188}\text{Os}$ of the hydrothermal sulfide isochron is 0.36 ± 0.1. Calculated $^{187}\text{Os}/^{188}\text{Os}$ initials for the magmatic magnetite in the intrusive rocks range from 0.2 - 0.41, and the initial $^{187}\text{Os}/^{188}\text{Os}$ ratios for sulfide from Bronce mine, a small satellite of the Candelaria main orebody, is 0.33. All of the initial values are similar and too radiogenic to be derived solely from the mantle. The similarity in $^{187}\text{Os}/^{188}\text{Os}$ initial values of the ore and magmatic oxides suggest that the granitoid plutons were the source for metals in the Candelaria district.

Introduction

The Candelaria Cu-Au deposit (470 Mt at 0.95 % Cu, 0.22 g/t Au, and 3.1 g/t Ag) south of Copiapó, Chile (Fig. 2.1), belongs to a class of deposits characterized by abundant Ti-poor iron oxide mineralization referred to as iron oxide (Cu-U-Au-REE) class or categorized as low sulfur Cu-Au deposits (e.g., Hitzman et al. 1992; Barton and
Iron oxide-rich Cu-Au deposits constitute a major Cu resource with potential for additional economic concentrations of U, LREE and other metals (Hitzman et al., 1992). Their genetic relationships with contemporaneous plutonic rocks are controversial. There are two competing end member models: a magmatic and a non-magmatic model (Fig. 2.2). The magmatic model postulates magmatic metal and sulfur-bearing fluids exsolve from crystallizing magma(s) and deposit metals in the adjacent country rocks (e.g., Gow et al., 1994; Rotherham et al., 1998; Williams, 1998; Williams et al., 1999). The second model requires an evaporite-derived, thermally driven fluid to leach and re-deposit metals and sulfur (Battles and Barton, 1995; Barton and Johnson, 1996; Barton et al., 1998; Ullrich and Clark, 1999).

Both of these models have been proposed for describing the metallogenesis of Candelaria (e.g. Ulrich and Clark, 1999, Marschik et al., 2000). Here we provide genetic and geochronologic constraints on these models through Re-Os isotopes. The results support a magmatic origin for the iron oxide Cu-Au mineralization at Candelaria, however do not exclude the nonmagmatic model.

The major advantage of using Re-Os isotopes on ore minerals is that timing and genetic information can be obtained from the ore rather then 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 metallogenesis because Re is more incompatible then Os during mantle melting (Walker et al., 1989). Crustal materials therefore have larger Re/Os ratios, and develop a higher $^{187}\text{Os}/^{188}\text{Os}$ with time compared to the mantle (Walker et al., 1989) as $^{187}\text{Re}$ decays to $^{187}\text{Os}$ with a half-life of
about 42 Ga. The current chondritic mantle $^{187}\text{Os}/^{188}\text{Os}$ is approximately 0.13 (Meisel et al., 1996). Initial ratios greater than the chondritic mantle can indicate a crustal source for Os.

Molybdenite contains orders of magnitude more Re than the common sulfides and effectively no initial radiogenic $^{187}\text{Os}$ (Luck and Allegre, 1982, McCandless, 1993; Stein et al. 1998). Therefore, it can be used as a high-precision geochronometer (Stein et al. 1998 a, b).

**Geologic context**

The Candelaria deposit is hosted in volcanic and volcanoclastic rocks of the Early Cretaceous Punta del Cobre Formation (> 1000 m) that underlies marine carbonate rocks of the Chañarcillo Group (up to 2000 m; Corvalán, 1974). These rocks represent a facies transition of a continental volcanic arc to the west and northwest and a shallow marine back-arc basin lying to the east (Fig. 2.1). Marine conditions commenced in the basin in Berriasian times (about 140 Ma) and ceased due to regional uplifted in late Aptian-Albian times (112 Ma; e.g., Segerstrom and Parker, 1959; Pérez et al., 1990; Jurgan, 1977, Unesco-IUGS International stratigraphic Chart 2000). Conglomerates, andesitic lavas, and pyroclastic rocks of the Cerrillos Formation (up to 4500 m) unconformably overlie the partly eroded rocks of the Chañarcillo Group (e.g., Segerstrom and Parker, 1959; Zentilli, 1974).

Granitoid plutons of the Copiapó Batholith intrude the back-arc sequence in the western part of the area (Fig. 1; Tilling, 1962, 1976). Near the Candelaria mine, the Copiapó Batholith consists of several dioritic-granodioritic to quartz monzonitic
intrusions (SiO₂ 50-68 wt. %). Potassium-argon ages of these intrusions range from 119 to 97 Ma (e.g., Zentilli, 1974; Arevalo, 1994, 1995). Recently conducted $^{40}\text{Ar}^{39}\text{Ar}$ analyses on biotite from a monzodiorite (Kmd) yielded a weighted mean plateau age of 111.5 ±0.4 Ma (Arevalo, 1999). The same study reports a hornblende isotope correlation age of 109.9 ±1.7 Ma and a biotite isotope correlation age of 109.9 ±0.4 Ma for a tonalitic pluton (Kt; Fig. 1).

Field relationships combined with these new $^{40}\text{Ar}^{39}\text{Ar}$ ages establish a rough time frame for the main intrusive phases near the Candelaria mine. These relationships show that a diorite (Khd) with a biotite K-Ar age of 111± 3 Ma (Sierra Atacama diorite; Arevalo, 1994) predates the tonalite (Kt) and quartz monzonite (Kap; Fig. 2.1). The latter has a tectonic contact with the monzodiorite (Kmd) to the northeast. The diorite (Khd) and quartz monzonite (Kap) are marginally affected by sodic-calcic ± K-feldspar alteration, whereas the monzodiorite (Kmd) is unaffected by this alteration and therefore younger. These field relationships suggest that the diorite (Khd) is the oldest of these four plutons for which we assume an age of 114 Ma (i.e., at the older end of the analytical error). This assumed age is the older limit of the quartz monzonite (Kap), which consequently is thought to have been emplaced between 114-111.5 Ma.

Mineralization

Candelaria is the largest of several iron oxide Cu-Au deposits that occur along the eastern margin of the Copiapó Batholith (Fig. 1). Candelaria was discovered in 1987 as
result of an exploration program around the Lar and Bronce mines that hosted small manto-like sulfide copper-gold orebodies. (Ryan et al. 1995). The Lar mine resides directly above the Candelaria orebody, whereas the Bronce mine is located in a different tectonic block that lies to the east. The Bronce block is separated from the block that hosts the ore of Candelaria by the north-northwest trending Bronce fault (Fig. 2.1). The Bronce and Lar mines are interpreted to represent satellites of the Candelaria orebody because of their proximity and similar ore mineralogy to Candelaria, however, no connecting feeder zone for the mineralization has been documented. Important mining is also taking place in the Punta del Cobre district, which is located about 3 km northeast of Candelaria. In the Punta del Cobre district, several small and medium size mines (e.g., Carola, Santos, and Socavón Rampa-Trinidad) extract copper ore from a number of geographically separated ore zones (e.g., Marschik and Fontboté, 1996). Combined estimated reserves of all iron oxide Cu-Au deposits in the Candelaria-Punta del Cobre area are in the order of 700-800 Mt of 1 % Cu.

Hypogene ore mineralogy at Candelaria consists mainly of magnetite chalcopyrite, and pyrite. Gold is commonly associated with chalcopyrite and pyrite (Ryan et al., 1995). Pyrrhotite, sphalerite, elevated concentrations of light rare-earth elements, and trace quantities of molybdenite and arsenopyrite are found locally in the orebody. Copper mineralization occurs as massive veins and breccias, discontinuous veinlets or stringers, and as roughly bedding-concordant manto-like bodies. Chalcopyrite-pyrite mineralization is superposed on biotite-quartz-magnetite alteration in volcanic and volcanoclastic host rocks and on massive magnetite bodies. The copper mineralization shows a close spatial and temporal relationship with post-magnetite calcic-amphibole alteration (e.g., Ullrich and Clark, 1999; Marschik et al., 2000).
Results of stable and radiogenic isotopes analyses are consistent with a magmatic fluid dominated hydrothermal system. Sulfur isotope ratios of sulfides from the Candelaria deposit and several other nearby deposits fall into a range of $\delta^{34}$SCDT values between −0.7 to 3.1‰ (Marschik et al., 1997b; Marschik and Fontbote, in review). This narrow range of near 0‰ $\delta^{34}$SCDT is consistent with magmatic sulfur, or with sulfur leached from igneous rocks. Oxygen isotope ratios of quartz associated with chalcopyrite from the Candelaria deposit are between 11.2 to 12.6‰ $\delta^{18}$OSMOW. Fluid inclusions in this quartz homogenize at temperatures from 370° to >440°C. The calculated isotopic fluid composition in equilibrium with this quartz at these temperatures is +5.9 to +8.9‰ $\delta^{18}$OSMOW (isotope fractionation factors of Friedman and O’Neil, 1977). These results are compatible with a fluid of magmatic origin or a non-magmatic fluid equilibrated with silicates at high temperatures. Lead isotope signatures of ore minerals from Candelaria and the Punta del Cobre district and plutonic rocks of the Copiapó Batholith largely overlap which is compatible with the hypothesis that there is a relationship between the intrusions and the mineralization (Marschik et al., 1997; Marschik and Chiaradia, 2000). This study also indicates that there is leaching of Pb (and possibly other metals) from the volcanic rocks along the batholith contact in the Candelaria-Punta del Cobre area.

**Age of Alteration**

Multiple analyses of alteration minerals produce ages that range from 110-116 Ma. The span of ages can be broken into 2 general periods, an older group of about 114-116 Ma and a younger group 110-112 Ma. The most precise ages of the older group are from hydrothermal biotite that accompanied main magnetite formation, and yield a $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of 114.1 ±0.7 Ma (all errors reported at ±2σ; Ullrich and Clark,
This biotite age is consistent with a $^{40}\text{Ar}^{39}\text{Ar}$ inverse isochron age of $114.9 \pm 1.0$ Ma for hydrothermal biotite from the biotite-quartz-magnetite alteration in the Santos mine (Punta del Cobre district). A less precise $^{40}\text{Ar}^{39}\text{Ar}$ total fusion age of $114.6 \pm 1.6$ Ma from ore-related biotite from the Resguardo mine (Punta del Cobre district), and a Rb-Sr isochron age of $116.8 \pm 2.7$ Ma calculated from seven whole rock analyses (Marschik et al., 1997a) are identical with the two previous ages. This suggests that the biotite quartz magnetite alteration of Candelaria and the Punta del Cobre district have the same age.

In general, younger alteration ages appear to be associated with sulfide mineralization. For instance, amphibole from Candelaria associated with chalcopyrite gave an $^{40}\text{Ar}^{39}\text{Ar}$ plateau age of $111.7 \pm 0.8$ Ma (Ullrich and Clark, 1999). An $^{40}\text{Ar}^{39}\text{Ar}$ total fusion weighted mean age of $111.6 \pm 1.4$ Ma (2 analyses) for biotite ore-related from the Resguardo mine and two $^{40}\text{Ar}^{39}\text{Ar}$ correlation ages of $111.0 \pm 1.4$ Ma and $110.7 \pm 1.6$ Ma for biotite from mineralized host rocks at Candelaria (Arevalo et al., 2000) are identical with this amphibole age.

Samples and Analytical Techniques

Hydrothermal magnetite, chalcopyrite, and pyrite from Candelaria, and pyrite from Bronce mine were chosen for Re-Os analyses. The samples were wrapped in paper, crushed, sieved, and magnetic separations were conducted in order to obtain pure samples of each phase. Molybdenite was hand-picked from a amphibole-rich sample, and parts of this molybdenite were analyzed by electron microprobe to determine if there was alteration. Diorite (Khd), monzodiorite (Kmd), and tonalite (Kt) samples (Fig. 2.1) were crushed, sieved, and the magnetic fraction was separated for analyses.
Concentrations of Re and Os were determined by isotope dilution. Analyses were conducted on a negative thermal ionization mass spectrometer (N-TIMS). All samples were dissolved by the carius tube method (Shirey and Walker, 1995), and distilled by methods similar as described in Mathur et al. (2000). A reverse aqua regia solution was used for all samples except the magnetites. In order to achieve complete dissolution of the magnetites, a 2:1 mixture of nitric and hydrochloric acids was used rather then the normal 3:1 mixture. Sample preparation and loading techniques for are from Creaser et al. (1993).

Results

The molybdenite samples yield mineralization ages of 114.2 ± 0.6 and 115.2 ± 0.6 that coincide with radiometric ages for the early potassic alteration at Candelaria and in the Punta del Cobre district (Marschik et al., 1997; Ullrich and Clark, 1999).

McCandless et al. (1994) and Suzuki et al. (2000) have evaluated molybdenite for the possible disturbance of the Re-Os system by alteration. Their results indicate that Re and Os can be mobilized in common low temperature ore forming solutions. The unaltered appearance of the molybdenites at the microprobe level and the reproducible age of this study indicates that these most likely reflect the age of mineralization rather then alteration ages. Stein et al. (1998 a) suggest plotting molybdenite data on isochron plots that simply use the concentration of daughter $^{187}$Os versus parent $^{187}$Re on the axis of isochron plots. If the data are plotted accordingly, the same age is obtained.

Hydrothermal magnetite, chalcopryite, and pyrite from the Candelaria orebody have concentrations of Os and Re of 9-23 ppt (parts per trillion $10^{-12}$g/ g) and 0.4-4 ppb
(parts per billion, $10^{-9}$ g/g) respectively (Table 2.1). Procedural blanks for the study varied from 1.5-2.7 ppt Os and 25-35 ppt Re. The $^{187}\text{Os}^{188}\text{Os}$ of the blank remained constant (~0.175). Since the greatest source of error in the analysis is the concentration of the Os blank, errors for the magnetites and sulfides are calculated by varying the blank concentration. Data treatment is described in Mathur et al. (2000,a). The isotopic ratios of the hydrothermal ore minerals form an isochron with an age of 110 ± 9 Ma (MSWD 1.4) with an initial $^{187}\text{Os}^{188}\text{Os}$ ratio of 0.36 ± 0.1 (Fig. 2.3). The samples from Bronce mine have more Os (about 1 ppb) and Re (16 ppb) compared to the Candelaria ore. The initial $^{187}\text{Os}^{188}\text{Os}$ ratio calculated is 0.33 assuming a mineralization age of 114-115 Ma which is the age molybdenites from Candelaria.

The magmatic magnetites contain between 40-200 ppt Os and 0.8-4 ppb Re. Initial $^{187}\text{Os}^{188}\text{Os}$ ratios calculated for the magnetite range from 0.2-0.4. Mineral separations of magnetite from the intrusive rocks were used because the bulk of Re-Os most likely resides in the magmatic sulfides associated with the magnetite or in the magnetite itself. However, the concentration reported here is an overestimation of the total Re-Os budget of the whole rock.

The initial $^{187}\text{Os}^{188}\text{Os}$ values were calculated by using $^{40}\text{Ar}^{39}\text{Ar}$ ages of Árvalo (1999) for the corresponding intrusions: tonalite (Kt; 109.9 Ma), monzodiorite (Kap; 111.5 Ma). Field relationships illustrate that the tonalite (Kt) and the quartz monzonite (Kap) are younger than the hornblende diorite (Kmd), therefore an age of 114-116 Ma was assumed for Kmd.
Discussion

The Re-Os data illustrate that mineralization is closely coupled with the cooling and crystallization of the nearby intermediate plutonic rocks. Figure 2.4 shows Re-Os and previously published radiometric ages from the Candelaria district. The diagram demonstrates that the Re-Os ages obtained from the molybdenite, and the pyrite, chalcopyrite, and magnetite isochron coincide with the previous geochronologic determinations.

The Re-Os isochron from hydrothermal magnetite, chalcopyrite, and pyrite has an error that spans the range of previous radiometric ages. As mentioned above, copper mineralization overprints the main magnetite mineralization. Individual magnetite, and chalcopyrite isochron plots do not distinguish these two mineralization stages.

Molybdenite is paragenetically overlapping with the main copper mineralization (Marschik et al., 2000; Ullrich and Clark, 1999), therefore the molybdenite ages pinpoints mineralization to have occurred at 114-115 Ma.

The Re-Os molybdenite age reported above would indicate that the bulk of mineralization is coincident with the older $^{40}\text{Ar}/^{39}\text{Ar}$ alteration ages. The two samples were collected from different parts of the mine and the similarity of their ages most likely reflect the reliability of the age as suggested by Suzuki et al. (2000), and Stein et al. (1998).

The initial $^{187}\text{Os}/^{188}\text{Os}$ ratio for magmatic and hydrothermal magnetite, chalcopyrite, and pyrite is around 0.3, and reveals that there is a mantle and crustal component in the magma and the ores. Figure 2.5 illustrates that there is a crustal
contribution to the magmatic and mineralizing system. Possible radiogenic sources for Os in magmas that occur in arc/back arc environments are the upper/lower continental crust (which was relatively thin at this time), the subducting slab and its accompanying sediments, and/or a metasomatized mantle (Roy-Barman et al., 1997; Brandon et al., 1996, Esser and Turekian, 1993).

Figure 2.5 also shows that the initial Os ratios for the magmatic magnetites, the hydrothermal ore minerals in Candelaria, and the samples from the nearby Bronce mine, are similar. This indicates that the source of Os for the magma, the main orebody, and its satellite are the same. The initial $^{187}\text{Os}/^{188}\text{Os}$ ratios of the ore ($0.36 \pm 0.1$) overlap with those of the diorite ($0.25 \pm 0.01$). In addition, the molybdenite age of $\sim 114$ Ma is similar to the assumed age of $114$ Ma of the diorite (Khd). These results support the hypothesis that mineralization is genetically related to the dioritic phases of the Copiapo Batholith (Marschik and Fontboté, 1996).

This Re-Os evidence adds to other isotopic evidence that suggests a magmatic source for the ores such as:

1. The narrow range of sulfur isotope ratios in the sulfides near $0\%e \delta^{34}\text{S}_{\text{CDT}}$.
2. Oxygen isotope data, which combined with microthermometric data are consistent with predominately magmatic fluids during the main copper mineralization.
3. The overlapping lead isotope signatures of ore minerals from Candelaria and the Punta del Cobre district and plutonic rocks of the Copiapo Batholith.

In order to further explore the evidence for a predominantly magmatic or non-magmatic fluids in the ore forming system, a simple mixing calculation for the Re-Os
contents of hypothesized fluids involved is relevant. However predicting the Os concentration and \(^{187}\text{Os}/^{188}\text{Os}\) isotopic ratio of the magmatic fluids and the fluids derived from sedimentary rocks is difficult. The main problem is estimating the Os concentration of the brines and magmatic fluids.

Suzuki et al. (2000) illustrated that Re and Os are mobile in typical lower temperature hydrothermal solutions because they could alter molybdenites in saline solutions (i.e. 0.1 M NaCl) at 180°C within 20 days. Further evidence of Os mobility in low temperature solutions has been seen in the fluctuation of the \(^{187}\text{Os}/^{188}\text{Os}\) composition of sea water and river waters with time (Sharma et al., 1997; Puecker-Ehrenbrink and Blum, 1998), however the concentration Os in the water is very dilute (femtagram level).

In the case of Candelaria, a hypothetical evaporite-derived brine would probably have a temperature of >120°C assuming that this fluid penetrated to a depth of 3 km (the depth at which mineralization occurred) and that the basin had a minimum geothermal gradient of 40°C/km (Fig. 2.2; model b). This fluid would possibly acquire an Os isotopic signature close to that of the penetrated sedimentary rocks. Shales, mudstones and limestones (Raivizza and Turekian, 1989; Ravizza, 1993; Esser and Turekian, 1993; Sign et al., 1999, Chesley et al., 2000) have radiogenic signatures and typically have concentrations of Os that exceed 100ppt. This is a conservative estimate considering fluids can contain more than 1 ppb Os (Xiong and Wood, 2000).

Determining the isotopic ratio present in this basinal brine is also difficult. Since the limestones, evaporites, shales, and mudstones from which the brine could have originated are in the range of 135-115, the isotopic initial value of these marine sediments
most likely resembles seawater at the time of deposition. Cohen et al. (1999) determined that the $^{187}\text{Os}/^{188}\text{Os}$ of seawater at the end of the Jurassic and the beginning of the Cretaceous to be about 0.8. Assuming this initial ratio and a modest Re/Os ratio for marine sedimentary rocks of about 300 (Cohen et al. 1998) at the time of ore deposition, the sedimentary rocks would have a measured $^{187}\text{Os}/^{188}\text{Os}$ of about 1. This means that if the fluid is in isotopic equilibrium with the sediments the Os isotopic ratio would 1, and would most likely be detected in the ores.

Although there is evidence for mobility of Os in hydrothermal solutions that were involved in the genesis of Candelaria, our data does not provide conclusive proof to unequivocally illustrate that magmatic fluids were the dominant feature of this hydrothermal system. For instance, a saline evaporitic brine at low temperature may not have acquired Os from the carbonate and shaley rocks of Chañarcillo Group in route to the cooling intrusion (Fig. 2.2; model b). Once close to the heat source, the brine may acquire Os from the volcanoclastic rocks of the Bandurrias Group that are genetically related to the batholithic intrusions. Therefore, this model could explain the similarities in Os isotope signatures.

An important aspect of the data presented here is the concentration of Os and Re in the sample from Bronce mine, which has 1 ppb Os and 16 ppb Re. These high concentrations for both elements could be representative of a zonation found in which Re and Os behave like the noble metals such as Au. Gold tends to be present in higher concentrations at the upper parts of the ore deposit. Importantly, the initial $^{187}\text{Os}/^{188}\text{Os}$ value of Bronce ore is similar to that of Candelaria and the those of the granitoid rocks,
thus indicating essentially the same source. This is opposite to what was found in
Grasberg, in which a clear mixing relationship is seen with magmatic and sedimentary
sources (Mathur et al., 2000b). Perhaps, the correspondence between the periphery ores
and magmas provides stronger evidence for a magmatic source.

Marschik and Fontboté (1996) genetically interpreted the mineralization to
occupy a transitional position between the magnetite(-apatite) ores of the Chilean iron
belt and Andean porphyry copper deposits. Figure 2.6 is a concentration diagram
illustrating the average concentration of Re and Os in these two types of systems. The
elevated Os concentration in the Candelaria ore would suggest that this system is
different from ‘typical’ Andean porphyry coppers. However, the other end-member of
ore deposits to which Candelaria could be genetically related, i.e., magnetite-apatite
deposits of the Chilean iron belt, have not been documented in terms of Re-Os contents.

Conclusions

Re-Os ages from molybdenite of 114.2-115.2 Ma are consistent with the older
radiometric ages (114-116 Ma) from alteration minerals associated with iron oxide
mineralization. The isochron age of 110 ± 9 Ma derived from hydrothermal magnetite,
chalcopyrite, and pyrite is identical within error with the Re-Os molybdenite and
previously published radiometric ages of the district.

Calculated initial $^{187}$Os/$^{188}$Os values have important petrologic and metallogenic
information. Initial $^{187}$Os/$^{188}$Os of magmatic magnetite from the granitoid plutons of the
Copiapó Batholith range from 0.2-0.4. This implies that these magmas originate from
crustal and mantle sources. Initial $^{187}$Os/$^{188}$Os from hydrothermal magnetite,
chalcopyrite, and pyrite from Candelaria and Bronce are between 0.26-0.46 and overlap with those of the granitoids. The initial $^{187}\text{Os}/^{188}\text{Os}$ ratios suggest the same source of Os for the iron oxide Cu-Au mineralization at Candelaria and the plutons of the Copiapó Batholith. The data is compatible with the hypothesis that predominately magmatic fluids caused the main mineralization at Candelaria, but does not exclude alternative models that invoke nonmagmatic fluids. The average concentrations of Re and Os in Candelaria ore are distinctly different than what is found in Chilean porphyry copper deposits.

Acknowledgments:

We thank Compañía Contractual Minera Candelaria, Phelps Dodge Exploration, Chile for their support. We especially thank W. Martin for his stimulating discussions about the project. Also, we thank M. Baker and J. Chesely for their assistance in the laboratory. Analytical work was supported by the National Science Foundation Grants EAR 9708361, and EAR 9628150, and a instrumentation grant from the W. M. Keck Foundation.

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<table>
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<tr>
<th>Sample</th>
<th>Phase</th>
<th>Re (ppt)</th>
<th>Os (ppt)</th>
<th>(^{187}\text{Re}/^{188}\text{Os})</th>
<th>(^{195}\text{Os}/^{188}\text{Os})</th>
<th>(^{188}\text{Os}/^{198}\text{Os}_0)</th>
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<td>Cand-3a</td>
<td>mag., pyr.</td>
<td>428</td>
<td>9</td>
<td>298 +/- 31</td>
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<td>mag., pyr.</td>
<td>335</td>
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<td>0.36 +/- 0.10</td>
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<td>1592</td>
<td>13</td>
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<td>1.77 +/- 0.123</td>
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<td>17</td>
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<td>1326</td>
<td>61 +/- 0.61</td>
<td>0.4459 +/- 0.001</td>
<td>0.33 +/- 0.005</td>
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<tr>
<td>Cand moly-2</td>
<td>moly.</td>
<td>73 ppm</td>
<td></td>
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<td>114.2 +/- 0.6</td>
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Figure 21.- Geologic map of the Candelaria area (modified from Tilling, 1976), and cross section through the Candelaria deposit ages for batholithic rocks from Arévelo (1994, 1999).
Figure 2.2- End-member models for the Candelaria iron oxide Cu-Au mineralization. The Chañarcillo Group are limestones and shales with radiogenic Os signatures. The Bandurrias Group (including the Punta del Cobre Formation) are volcanoclastic and volcanic rocks related to Early Cretaceous magmatism with Os signatures possibly similar to the Copiapó batholith. Model a) represents a magmatic fluid-dominated system. Model b) represents deep circulating evaporitic brines that acquire limestone/shale Os signatures at elevated temperatures. These fluids are not significantly modified in their Os contents when they subsequently flow through the volcanoclastic rocks of the Bandurrias Group. Model c) represents a relatively cooler fluid that does not initially acquire the Os signature of the marine back arc deposits, however, the fluids become heated when they approach the cooling plutons and leach Os from the volcanoclastics rocks of the Bandurrias Group.
Age: 110 +/- 9 Ma
MSWD: 1.363

Initial = 0.36 +/- 0.1

Figure 2.3- Re-Os isochron for chalcopyrite, pyrite, and magnetite
Younger Ar ages, possible post-main mineralization (hydro)thermal event

Figure 2.4-Compilation of geochronologic data on the batholithic rocks, ore, and alteration minerals from the Candelaria district
Figure 2.5- Comparison of the $^{187}\text{Os}/^{188}\text{Os}$ initial ratios for the ores and magmatic oxides of Candelaria
Figure 2.6: Average Re and Os concentrations of ores from Candelaria (circle) and Andean porphyry copper deposits (rectangle).
Chapter 3- Different crustal sources for Au-rich and Au-poor ores of the Grasberg Cu-Au porphyry deposit

Abstract

The Grasberg is a porphyry copper deposit that is crosscut by a second stage mineralization which is greatly enriched in gold. Sulfides from the porphyry-type event yield a 2.9 +/- 0.3 Ma Re-Os isochron that agrees with published geochronology. The initial $^{187}$Os/$^{188}$Os ratio of the isochron is 0.56 +/-0.02, and implies a significant crustal component for the source of Os and by inference the other base metals. The samples from the crosscutting secondary event do not form an isochron, but form a mixing line with the older porphyry style mineralization as one of the end members and a very radiogenic end member possibly shale. The initial $^{187}$Os/$^{188}$Os ratios from samples of the second event range from 0.81-1.26 and correlate with gold content. The most radiogenic samples have the highest gold. 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, that may have been pre-enriched by sedimentary processes. The gold derived from these sources is concentrated by magmatic/hydrothermal systems. The requirement of a sedimentary source for gold to produce hydrothermal gold deposits has been debated for decades and this study provides strong support for the model.

Introduction

The source of gold in ores is a significant and long-standing question that has been addressed historically in qualitative ways. The importance of the source problem is
two-fold, addressing first, questions of geochemical processes of crustal evolution and history, and second, the question of whether metal-"source" terranes, characterized by pre-enrichment of certain metals, should be utilized in resource evaluation. Conventional thought has viewed metals as indigenous to the igneous intrusions' source of magma generation. Contrary to this perspective, other hypotheses consider metal as derived from volcanic and sedimentary rocks of the crust (Krauskopf 1967; Noble 1970; Burnham 1959) in which the intrusion resides, remnants of deep metallogenic heterogeneity in the mantle (Sillitoe 1972), or the melted subducted oceanic crust (Zartman 1974).

Gold has been of particular interest because of its occurrence in a wide variety of styles of ore deposits and its time-enduring habits of occurrence. Titley (1991) reviewed the occurrence of gold in association with Phanerozoic sedimentary rocks and proposed that there is pre-enrichment of gold in Lower Paleozoic and Mid- to Upper Mesozoic strata, which may be regenerated and enriched in younger deposits by a variety of crustal processes. This general notion is not new. Boyle (1986) and Sangster (1992) reviewed the occurrence of gold in turbidite successions and proposed that gold-bearing ores of many regions were derived from pre-enriched source beds through a process that involves the devolitization and transport of gold from the sedimentary rocks through metamorphism.

Here we address the origin of gold in large intrusion-centered copper deposits, the "porphyry copper deposit" of common usage. These deposits form along active continental margins and on island arcs. They are the result of the shallow (6km) emplacement of small plutons or pluton complexes (~4km² area), commonly associated
with volcanic centers. The metal deposits originate from the cracking of large volumes of rock and the development of convective fluid flow associated with the thermal and mechanical effects of emplacement and cooling of plutons at shallow levels in the crust (Norton 1982). The sources of copper and gold present in deposits of this sort are conventionally believed to be similar and acquired from magmatic fluids.

We present the result of studies of the Grasberg deposit in West Irian Jaya where isotopic evidence (Housh and McMahon 2000) allows metallogenic interpretation of porphyry magmas that originated from melted Australian continental crust. The magmas have cross cut and potentially involved a succession of Proterozoic and lower Paleozoic strata of the sort described here (Titley 1991; Boyle 1986; Sangster 1992) at some great depth (>4km) beneath the deposit. We have used the Re-Os isotopic system to determine if strata of Phanerozoic age may have contributed to the high gold content of the Grasberg ores, thereby testing the notion that there are potentially different sources for the base metals in certain types of mineral deposits. The source of gold as revealed by the Re-Os systems in the porphyry deposit of Lihir (McInnes et al., 1999), in the Bushveld layered mafic intrusion, and in the ancient basin of the Witswatersrand (Hart et al. 1989) indicated a single source for metals that involved the mantle or partially metasomatized mantle as a predominant source for gold.

The use and potential of the Re-Os isotopic system to trace the source of metals and determine mineralization ages in ore deposits are starting to be realized (Hart et al. 1989; McInnes et al. 1999; Mc Candless and Ruiz 1993; Stien et al. 1997, Frie et al. 1998; Mathur et al. 2000). $^{187}$Re decays to $^{187}$Os (with a half-life of 42.3 billion years) by

\[ \text{Re} \rightarrow \text{Os} \]
beta emission. Importantly, rhenium and osmium are concentrated in sulfide phases and permit geochronologic and genetic information to be obtained from the ore mineral rather than alteration silicates. Crustal and mantle reservoirs within the subduction zone environments develop distinct $^{187}$Os/$^{188}$Os ratios through time because crustal materials have higher Re/Os (Walker et al. 1989). Construction of isochron diagrams for these sulfides provide the age of mineralization, and the initial $^{187}$Os/$^{188}$Os value of the ore forming fluids. The initial $^{187}$Os/$^{188}$Os can be used to trace the source of Os, and by inference the other base metals, (Cu) which should have a similar geochemical behavior. In regard to Os similarities to Au, they are both noble metals, and believed to be soluble in similar types of aqueous solutions (Xiong and Wood 2000). Thus, the source of Os can be used as a proxy for the source of the metals in ore deposits.

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 (Freeport 1997). The ore deposit formed during recent magmatic events corresponding with the collision of the Australian and Indo-Pacific plates and occurs within the central mobile fold belt (Van Nort et al. 1991; McDonald et al. 1995) (Fig. 3.1). In general, the magmatic rocks of this ore deposit intruded highly deformed/ metamorphosed Proterozoic and Paleozoic through Cenozoic sedimentary rocks. The basement in this area is thought to be the Australian continental crust (McDonald et al. 1995). The intrusions consist of three porphyries (Dalam [oldest]- Main Grasberg Intrusion- Kali [youngest]) of diorite to quartz monzonite composition that intruded a succession of clastic and carbonate strata (Fig. 3.1). Housh and McMahon (2000) studied the geochemistry of the volcanic rocks in the
region and interpreted variable Pb ($^{206}\text{Pb}/^{204}\text{Pb} - 18.002-18.291$, $^{207}\text{Pb}/^{204}\text{Pb} - 15.535-15.616$, and $^{208}\text{Pb}/^{204}\text{Pb} - 38.395-38.744$), elevated Sr ($^{87}\text{Sr}/^{86}\text{Sr} - 0.70611-0.70707$), and negative Nd (eNd -10.3- -18.3) values as evidence of ancient (Proterozoic and Archean) crustal and depleted mantle components of the magmas in the district. The distribution of all metals in the deposit forms a horseshoe shaped aureole around the Kali intrusion, suggesting that this intrusion was responsible for the bulk of mineralization (Freeport 1998).

In general, two distinct mineralization events are recognized in the district. The older event associated with the porphyritic rocks and surrounding sedimentary rocks deposited traditional stockwork style porphyry vein, disseminated, and contact sulfide mineralization (Titley 1982). The second event crosscuts and borders the intrusions, and is characterized by massive, meter thick veins of pyrite, chalcopyrite, and magnetite. In order to study the sources of metals and relative timing of these events, samples were selected from drill core that intersected rocks carrying mineralization of both episodes (Fig. 3.1).

Techniques and Results

Separation of sulfides from the drill core for Re-Os analysis entailed wrapping each sample in paper (in order to reduce possible PGE contamination), crushing the drill core with a hammer, and hand picking the sulfides. Concentrations of Re-Os were determined by isotope dilution. Typically 0.5 –1.5-gram samples were loaded into a Carius tube and dissolved in a reverse aquaregia solution. The Os was extracted from the solution through a two-distillation process (Frie et al. 1998) and Re through column
chemistry. Samples were analyzed on a negative thermal ionization mass spectrometer.

The details of sample preparation and running procedures are recorded in (Creaser, et al. 1994, Ruiz et al. 1997). Procedural blanks for Os ranged from 0.9-1.6 picograms and Re 25-35 picograms, which were corrected for in this study. Gold analyses were conducted by fire assay.

All results are presented in Table 3.1. The concentrations of Re and Os for these samples range from 6-20 ppb (parts per billion, or $10^{-9}$ grams per gram) and 0.005-0.071 ppb respectively. On average, these samples contained 3.47 ppm (part per million, or $10^{-6}$ grams per gram) gold and are considered samples of ore with the lower concentration gold. Gold and copper usually follow a 1 to 1 ratio for this part of the mineralized ore body. The data yield an isochron with an age of $2.9 \pm 0.3$ Ma (MSWD 1.2) which agrees with previous age determinations of 3 Ma on alteration silicates (Freeport 1998). The initial $^{187}$Os/$^{188}$Os determined from the isochron is $0.56 \pm 0.02$ (Fig. 3.2). Errors for each analysis are calculated by changing the blank concentration between 0.9-1.6 picograms Os since this is the greatest source of error in the analysis. The $^{187}$Os/$^{188}$Os isotopic composition of the blank is constant and around 0.175. The fact that the data lie on an isochron plot with the correct age indicates that the ore-forming fluids were isotopically homogeneous in Os.

Concentrations of Re and Os for the massive sulfide samples are much greater, ranging from 36-140 ppb and 0.047- 1 ppb, respectively. Gold concentrations are also higher in this zone averaging 12.65 ppm. This is defined as the gold rich ore because there is a relative increase in gold content without an accompanying increase in copper
content. Differences between the concentrations of Au, Re, and Os of the massive sulfides and porphyry vein style event are illustrated in Table 3.1 and Figure 3.3.

The five samples from different locations in the massive sulfide ore-body (Fig. 3.1) do not form an isochron; instead they form a mixing line (Fig. 3.4).

**Discussion**

*Older mineralizing event associated with the intrusion of the Kali:*

This event is characterized as the typical 'porphyry copper' style mineralization and alteration that evolved in a highly fractured stockwork. Sulfide samples from the high temperature alteration (biotite-orthoclase, quartz-sericite), the late stage covellite-pyrite mineralization, and the hydrothermal pyrites occurring in the Tertiary sedimentary rocks generate an isochron. The young age of the deposit and the analytical error obtained from an isochron constructed with sulfides from the biotite-orthoclase and quartz-sericite alteration zones suggests that the duration of mineralization in the Grasberg ore body was less than 600,000 years. This implies that the various biotite-orthoclase, quart-sericitic, and late stage covellite-pyrite alteration/mineralization phases occurred within this geologically short period.

Sulfides from different silicate alteration events in the Dalam intrusion and the Tertiary sedimentary rocks lie on the same isochron. This indicates a similar source of metals for sulfides regardless of the associated silicate alteration assemblages or the host rocks.

Inasmuch as the chondritic mantle \(^{187}\text{Os}/^{188}\text{Os}\) ratio is close to 0.13 (Walker et al. 1989; Meisel et al. 1996) the initial \(^{187}\text{Os}/^{188}\text{Os}\) value of the sulfides at about 0.56
indicates a significant crustal component for the Os, Cu, and Au. Possible radiogenic sources in the subduction environment are the descending oceanic slab (and accompanying sediments) (Roy-Barman et al. 1998), the upper/lower continental crust (Esser, and Turekian 1993), and a partially metasomatized mantle wedge (Brandon et al. 1996; McInnes et al. 1999). Simple two component mixing models using chondritic (Meisel et al. 1996) mantle with the mean lower crustal values from Proterozoic/Archean Northern Australian continental crust (Saal et al. 1998) that exists beneath Grasberg suggest at least 40% of the metals could have been derived from a radiogenic ancient lower crust. The relative proportion of crustal metals increases drastically if a lower concentration source such as the oceanic slab is considered. Regardless of the radiogenic source hypothesized, the amount of crustal metals present in the sulfides in the Grasberg ore body is significant. The radiogenic $^{187}$Os/$^{188}$Os isotopic signature of the metals combined with the extremely negative $\varepsilon$Nd and elevated $^{87}$Sr/$^{86}$Sr values for the magmas (Housh and McMahon 2000), suggests a model for this mineralizing event in which most of the metals could have been derived from a magma that had extensive interaction with the Proterozoic/Archean lower crust.

**Younger massive sulfide event:**

The massive sulfide ore bodies and their relationship to the porphyry mineralization remain enigmatic. Models for the mineralization range from fluids derived from a hidden porphyry, which migrate along previous fractures, to a late stage fluid associated with the porphyry intrusion (Titley 1996). Our Re-Os results indicate that the fluids responsible for precipitating the sulfide minerals of the massive sulfide had
evolving $^{187}\text{Os}/^{188}\text{Os}$ isotopic ratios. Figure 3.3 illustrates the difference between these two mineralized systems by a sharp isotopic and metal grade boundary between the massive sulfide and the main mineralizing event. Gold contents in this zone increase significantly without appreciable changes in copper abundance. The data (Fig. 3.3) indicate that the source of metals responsible for enriching the outer surrounding rim of mineralization in the ore deposit contained more gold, and Os.

The $^{187}\text{Os}/\text{Os}$ versus Os concentration (Fig. 3.4) trend suggests a relationship between the fluids that precipitated the main stockwork mineralization and the massive sulfide. In order to access relative proportions of crustal materials, a radiogenic source rock with a high concentration of common Os must have been accessed by the fluids or incorporated into the melt. There are few reservoirs in the geologic rock record that have appreciable concentrations of radiogenic Os. Brooks and others (Brooks et al. 1999) noticed a trend that higher concentration materials such as the mantle (1-10ppb) have lower Re/Os ratios (less then 1) and unradiogenic Os signatures. Lower concentration materials (0.5-0.05 ppb) have higher Re/Os ratios (>10) and radiogenic Os signatures. None of the reservoirs reported in these studies provide an end member with enough Os and a radiogenic signature to resolve the source of the high-end member on the mixing array present in the Grasberg sulfides.

Recent work on black shales (Ravizza et al. 1989; Ravizza et al. 1991; Horan et al. 1994) indicates that concentrations of Re-Os range from 20-300ppb and 0.1-13 ppb respectively. The concentration of these elements in black shales varies significantly compared with other geologic materials. However, two studies have found the higher
end concentrations of Re-Os in black shales of Precambrian and Devonian age sedimentary units (Horan et al. 1994; Sign et al. 1999). Van Uffort (1996) noted metamorphosed black shale equivalents in the sedimentary succession present in the Phanerozoic crust in which the Grasberg porphyries intruded. As Os concentrations and \(^{187}\text{Os}/^{188}\text{Os}\) in modern shale (Ravizza and Turekian 1992) are relatively uniform, these metamorphosed Precambrian and Devonian shales provide a plausible Os source at Grasberg. Simple mixing calculations between the initial radiogenic porphyry signature and the Devonian or Precambrian shales indicates at least 30% black shale component for the low concentration Os and Au end members. The proportion of the black shale component in the ores increases significantly when attempting to resolve the higher concentration radiogenic end members.

These data suggest that the fluid precipitating the massive sulfide have a component of the original porphyry and fluids that had possibly leached metals from the black shales in the lower crust. The Re-Os data support a model in which the porphyry intruded with its own Os isotopic signature, and as the system cooled fluids interacted with, and acquired metals from, metalliferous rich metamorphosed black shales present in deeper portions of the Phanerozoic middle crust. Perhaps a change in the fluid pH and temperature during metallogenesis invoked different chemical reactions with the host rock, thereby making gold more soluble and allowing it to enter the mineralizing system.

This is the first quantitative evidence of a process that extracts gold from surrounding sedimentary rocks during the genesis of an ore deposit. Inasmuch as the fluids that mineralized the massive sulfide were distinctly heterogeneous, and not
analogous to the fluids associated with the main intrusion, models ascribing the massive sulfide to a hidden porphyry at depth are unlikely.

**Conclusions**

This study provides geochemical evidence for the presence of crustal, and more importantly, sedimentary rocks as an essential source that enriches some of the metals in a porphyry copper ore deposit. Titley (1991) observed that formation of many gold deposits might be closely linked with crustal units that contain turbiditic sediments of Paleozoic and Cenozoic age. The Re-Os data from the Grasberg suggests that these kinds of rocks could be the source of metals for this deposit. Therefore, the relevance of this study is that it numerically illustrates the influence of the lower and middle continental crust during porphyry copper genesis. Specifically, it highlights two sources for the bulk of copper and gold in porphyry copper hydrothermal environments, and suggests that the interaction of the hydrothermal system with specific units in the crust produce gold rich ore.

**Acknowledgements:**

The studies reported here are part of the graduate research programs of Mathur and Gibbins. Analytical work was supported by the National Science Foundation Grants EAR 9708361, and EAR 9628150, and a instrumentation grant from the W. M. Keck Foundation. We thank Freeport McMoRan Copper and Gold, Inc. for providing assistance and support of the fieldwork, and permission to publish this information. The authors also would like to thank Jon Patchett, Chuck Brannon, Rick Carlson and an anonymous reviewer for their constructive comments on earlier drafts of this paper.
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<th>Re ppt</th>
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<th>187Re/188Os</th>
<th>187Os/188Os</th>
<th>187Os/188Os</th>
<th>Au (ppm)</th>
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Table 3.1- * Indicates values used to construct isochrons, error calculation is discussed in text, and isochron statistics were determined using algorithms of York [40]. All numbers following or associated with samples reflect drill core and depths of drill cores. Location of samples is labeled in the mineralization column. Abbreviations represent the dominate phase in the sample analyzed py = pyrite, cpy = chalopyrite, mag. = magnetite, m.s. = massive sulfide, Ter. sed. = Tertiary sediments, biot.-ortho. = indicates sulfides taken from the biotite-orthoclase alteration silicates, quartz-ser. = indicates sulfides taken from the quartz-sericite alteration silicates. All Au analysis done by fire assay techniques of Jacob’s Fire Assay, Tucson AZ.
Figure 3.1- Location and generalized section of the profile sampled in the southwest quadrant of Grasberg intrusive complex. The cross section illustrates the location of each sample with respect to alteration and host lithology. Solid circles indicate samples from the initial porphyry style mineralization, and X indicate samples taken from the younger massive sulfide event.
Figure 3.2- Isochron plot of the data from the porphyry style mineralization event, ages and initial values were calculated from algorithms of York, 1969.
Figure 3.4- Chemical mixing diagram, the solid square represents the average concentration and initial $^{187}\text{Os}/^{188}\text{Os}$ value of the main porphyry style-mineralizing event, whereas the darkened circles represent the average concentration and initial $^{187}\text{Os}/^{188}\text{Os}$ values from various samples in the massive sulfide event.
Figure 3.3- Concentrations of element along tested drill core GRS37194. Solid line indicates Os concentration, and X on the line indicates sample position, with the $^{187}\text{Os}/^{188}\text{Os}$ labeled. The dotted line represents the Cu concentration in %, and dashed line indicates the Au concentration in parts per million.
Chapter 4- Re-Os-isotopes applied to the high and low sulfidation epithermal gold deposits near Bucaramanga, northeastern Colombia

Abstract

The epithermal gold mineralization near the town of Bucaramanga, Colombia is spatially associated with a dacitic porphyry of Upper Cretaceous to Early Tertiary age. Two mining districts in the vicinity of Bucaramanga, the California district and the Vetas district, host high-sulfidation style mineralization and low-sulfidation style mineralization, respectively. Re-Os isotope systematics were used on sulfide-gold rich, gravity concentrates in an attempt to determine the age of both the epithermal deposits and the possible genetic relationships between the porphyry and the epithermal mineralization. The concentration of Os for both systems is relatively uniform ranging from 20 to 35 parts per trillion (ppt), whereas the Re concentrations varied significantly between the California system averaging 10 parts per billion (ppb) and the Vetas system averaging 140 ppb. The samples from the high sulfidation California deposit form an isochron with an age of 59 Ma ± 5 Ma (MSWD = 1.25), that is coeval with the age of the dacitic volcanism. The initial $\frac{^{187}Os}{^{188}Os}$ of the isochron is $1.18 \pm 0.09$, and indicates a predominately crustal source for the Os, and by inference gold. The samples from the Vetas low sulfidation system have very high Re/Os ratios and do not lie on the isochron.

These data reveal a difference between two epithermal systems related to one intrusion. The high sulfidation system is isotopically homogenous with respect to Re-Os, and probably represents mineralization closely linked with the high temperature volatiles/ fluids from the magma. In contrast, the Vetas system is in disequilibrium with respect to Re-Os, and illustrates mineralization not directly related to similar magmatic porphyry fluids.

Introduction:

Re-Os-isotopes have been widely and successfully used for dating and finding genetic information for various types of ore deposits (McCandless and Ruiz, 1993, Stein et al., 1998, Frei et al., 1998, McInnes et al., 1999, Mathur et al., 2000). These studies have provided important information regarding the source of metals and the timing of
mineralization. Re-Os concentrates in sulfide minerals, and can thus provide genetic information on the source of metals and the timing of mineralization. The advantage of using Re-Os isotopes is that information is obtained directly from the sulfide ore mineral, rather than by inferring chemical relationships from possibly unrelated alteration silicates. The system can be used as a chronometer because $^{187}$Re decays to $^{187}$Os. Source information can be obtained because the crust evolves a more radiogenic $^{187}$Os/$^{188}$Os signature in comparison to the mantle (Walker et al., 1989), which is presently about 0.13 (Meisel et al., 1996), with time. This behavior permits the recognition of distinct crustal and mantle reservoirs involved in metallogenesis, since the source of Os can be inferred as the source for similar chalcophile and platinum group elements (Xiong, and Wood 2000) such as copper and gold.

Here we explore the behavior of Re-Os in Au rich sulfides from epithermal systems associated with the intrusion of felsic magma. Epithermal systems form at relatively low temperatures (less than 300°C) and in shallow levels of the earth’s crust (less than 1-2km). They are commonly associated with volcanic rocks occurring in island and continental arc tectonic settings (Mitchell and Leach, 1991). These systems are classified into two broad categories based on geochemical and mineralogical properties of the mineralization and the wall rocks that are caused by different chemistries of the mineralizing fluids (Hedenquist & Arribas, 1999). High sulfidation (Hedenquist, 1987) or acid-sulfate type systems (Heald et al. 1987) form one end member of epithermal systems. They are characterized by reactive, oxidizing fluids with low pH, and have a large magmatic fluid component. The other end-member has been referred to as low sulfidation by Hedenquist (1987) and adularia-sericite by Heald et al (1987). Low sulfidation systems are characterized by near-neutral, reduced fluids that possibly have a more significant meteoric component (Hedenquist & Lowenstern 1994, Hedenquist & Arribas, 1999). Hedenquist’s (1987) terminology is based on the sulfidation state of the dominant ore mineralogy with enargite and fahlore as a major component of high sulfidation mineralization, and sphalerite and galena being more typical in low sulfidation mineralization. In comparison, Heald et al. (1987) use the wall rock mineralogy to
characterize the two epithermal end-members: while residual quartz, alunite and kaolinite are typical of the acid sulfate type, adularia, sericite, illite, calcite and chalcedony are commonly found in altered wall-rocks to adularia-sericite type mineralization. Other differences between the two end-members include the predominance of Cu and Au in high sulfidation systems as compared to Au, Ag, Pb and Zn in low sulfidation systems.

Our objective is to describe the genesis of these two types of extinct epithermal systems through using Re-Os isotopes. The issues addressed here are threefold. First and most importantly, Re-Os data will provide insight into the relative contributions of crustal and mantle source metals present in a continental arc epithermal setting. This question has been a source of contention in metallogenic studies. Chemical models have suggested that the crust could be a viable source for metals in these systems (Hedenquist, 1994). Specifically, Sillitoe (1989) illustrated that metal concentrations from active epithermal deposits are not sufficient to account for the total metal budget of these systems. The Re-Os data will help resolve these models by providing relevant source information. Second, the Re-Os data will assist in determining chronologic links between the two types of mineralization with respect to the intrusion of the porphyry. Our third objective is to identify differences or similarities in the source of metals among high sulfidation and low sulfidation mineralization presumably associated with the same intrusion.

Geology

The Bucaramanga gold mining district is located in the Santander Massif of the Cordillera Oriental in northeastern Colombia (Fig. 4.1). The Santander Massif displays a complex and poorly known metamorphic history. Figure 4.2 presents a generalized cross section of the area, and illustrates how mineralization is distributed in the deposits. Several phases of sedimentation followed by subduction and orogenic activities occur in the sequence.

The core of the Santander Massif consists of strongly tectonized, metamorphosed, and locally migmatized amphibolites, paragneisses, and granitic orthogneisses. Goldsmith et al. (1971) provide age data for metamorphism of basement rocks of the
Bucaramanga area using K-Ar methods on hornblende and biotite. Obtained ages range from Late Proterozoic of 950 Ma for hornblende-gneiss and through 680 Ma for biotite-gneiss to 450-413 Ma for granitic and dioritic orthogneisses that intrude the older paragneisses. More recent work on the geochronology of the area also reveal similar ages for the Santander Massif of about 800-900 Ma (Restrepo et al., 1997), and they interpret the Ar ages as affected by the Mesozoic volcanism. Polonia (1980) concludes that protoliths of the paragneisses range from greywackes through pelitic and psammitic rocks, and notes that limestone is lacking. This basement complex is in the Bucaramanga area collectively called the Bucaramanga Gneiss and is predominantly composed of metamorphosed sediments. Metamorphosed fossiliferous Devonian sediments locally cover it. Late Triassic through Jurassic continental sediments and felsic and andesitic volcanics unconformably overlie the Devonian metasedimentary rocks. These Mesozoic sediments are intruded by Triassic to Jurassic diorites and granites. The Mesozoic rocks are unconformably overlain by Cretaceous sediments, which develop from marine sediments in the Lower Cretaceous towards continental sediments in the Upper Cretaceous and Tertiary (Polania 1980).

A granodioritic porphyry in the California mining district intrudes these Cretaceous sediments. Uranium mineralization is hosted by the porphyry and has been described by Polania (1980). Sub-economic copper mineralization also seems to be associated with the porphyry. Previous age dating by the Nippon Mining Company (1967) yielded Upper Cretaceous to Early Tertiary ages for the porphyry.

Gold mineralization is located along faults cross-cutting sedimentary and igneous wall rocks to the dacite porphyry. In the California porphyry, highly altered dacitic porphyries and Mesozoic granites host a mineralized hydrothermal breccia. Mineralized veins also crosscut the altered dacite porphyry. Ore mineralogy consists of high-sulfidation assemblages in the California district. Alteration assemblages of this high sulfidation system consist of quartz-alunite and an element enrichment spectrum of Au, Cu, Ag, Te, Bi, As, Sb, and locally W.
In comparison, epithermal mineralization of the Vetas district consists of low sulfidation ore mineral assemblages, alteration mineralogies of sericite and adularia, and an element enrichment spectrum of Au, Ag, As, Pb and Zn. The Vetas district is located approximately 10km east of the California district and porphyry. Crustiform banding has been observed in hand specimens of Vetas. For a more detailed description of the geology of the Bucaramanga area refer to the BGR-CDMB report Etapa de diagnostico (Cooperacion Tecnica Colombo-Alemana 1998).

**Mineralogy**

The mineralogy of the epithermal gold deposits near Bucaramanga is highly diverse (Herb et al. 2000). In general, pyrite is the major ore mineral in both mining districts and comprises 80-90% of the mineralization in the California district and 90-95% of the mineralization in the Vetas district. In California Cu-sulfides, Cu-Bi-sulfides and various tellurides including gold-tellurides, gold-silver-tellurides, hessite, Te-bearing fahlore and native tellurium occur. Native gold is commonly enclosed in pyrite, fahlore and bornite. W-bearing phases such as Cu-W-Sulfides and huebnerite may be locally abundant and the alteration halo to mineralized veins consists of alunite, jarosite, kaolinite, and quartz. Polonia (1980) describes phyllic alteration and propylitic alteration in the dacitic porphyry as well. In the Vetas mining district, the telluride assemblage characteristic of California is very rare or absent. Pyrite is commonly intergrown with marcasite. Galena, tennantite, and fahlore may locally contribute significantly to the mineralization. Gold- and silver-tellurides are rare and gold occurs almost exclusively of native gold. Silver forms a silver-sulfide and locally occurs invisible in fahlore and galena. Sericite and adularia characterize altered wall rock mineralogy.

**Analytical procedures**

Sampling was undertaken during a technical cooperation project between BGR (Bundesanstalt für Geowissenschaften und Rohstoffe), Germany with the Colombian counterparts CDMB (Corporación Autónoma Regional para la Defensa de a Meseta de Bucaramanga), Compañía del Acueducto Metropolitano de Bucaramanga E.S.P.,
Ministerio de Minas y Energía and Gobernación de Santander during the Technical Cooperation Project *Reduction of the environmental contamination due to small scale mining in the catchment area of the Suratá River*. The samples for Re-Os analyses consist of gravity concentrates taken from active mines in the California and Vetas districts, namely from La Plata mine and El Volcan mine, respectively (Fig. 4.1). The concentrates of both mines consist mostly of pyrite (90-99%) and gold. In the concentrates of La Plata Cu-sulfides constitute up to 10% of the concentrate, whereas the El Volcan Mine concentrate contains almost exclusively pyrite commonly intergrown with marcasite, and gold. Magnetic separation was used on both samples in order to obtain a more sulfide rich sample for analysis. Molybdenite is rare in concentrates of both mining districts and has not been observed at the microscopic level in the concentrates.

One to two gram samples were digested by the carius tube method (Shirey and Walker, 1995) with the addition of hydrogen peroxide to ensure oxidation of samples. Re-Os was extracted through a distillation process similar to (Mathur et al. 2000, Frei et al., 1998). Os was further purified by a microdistillation (Roy-Barman et al., 1998), and Re was purified through a two stage column procedure. Samples were analyzed on an NTIMS at the University of Arizona; loading and running procedures are highlighted in Chesley and Ruiz (1998). The greatest source of error in our analysis is the concentration of the Os blank (its isotopic composition is uniform with a value of $^{187}\text{Os}/^{188}\text{Os}$ 0.175). Full procedural blanks for this study ranged from 1 to 2.8 picograms Os and 20-40 picograms Re, and are sufficient for this study. All reported errors on measured values in Table 1 represent the deviation about the mean, when the change of the blank is considered.

**Results**

The concentration of Os for both deposits ranged from 19-34 ppt (table 4.1). The Re concentration varied significantly between both deposits. The California system has a concentration of Re that ranges from 0.8-30 ppb, whereas the Vetas system has much higher concentrations of Re ranging from 123-153 ppb.
The California samples form an isochron with an age of 59.9 ± 5Ma (MSWD 1.25). This age overlaps with the Ar ages determined for the dacitic porphyry near the California system (Polonia, 1981). The isochron constrains an initial $^{187}\text{Os} / ^{188}\text{Os}$ ratio of 1.18 ± 0.09 (isochron statistics were determined from algorithms of York (1969)). The samples from the Vetas system do not form an isochron nor have any apparent mixing relationships. These samples plot to the extreme right of the California isochron (Fig. 4.3).

**Discussion**

These Re-Os data reveal three important insights into metallogenic history of the epithermal deposits associated with the California dacite porphyry.

1. The age of mineralization obtained from the Re-Os isochron for the high sulfidation California deposit is coeval with the dacite porphyry, and thus links mineralization with this hydrothermal system.

   Conventional models that describe high sulfidation ore genesis link ore deposition with degassing of a cooling intrusion and condensation of the oxidizing vapor into local groundwater (Hedenquist & Lowenstem, 1994). Arribas et al. (1995) illustrated, through K-Ar dating of alteration silicates, that the synchronous alteration/ mineralization of the geologically young Far Southeast porphyry and associated Lepanto epithermal copper-gold deposits occur in the island arc of the Philippines. The Re-Os age obtained here provides similar evidence that links the age of a porphyry and associated mineralization of an epithermal system. This age furthers the notion suggested by Arribas et al. (1995) that two deposit styles evolved from a single magmatic-hydrothermal event that possibly involved multiple intrusive events.

2. The source of the metals is predominately crustal, and we infer that surrounding crust or lower crustal materials contributed a large portion of the metal to the deposit.

   Conceptually, the model envisaged for high-sulfidation systems is one in which the deposit formed directly on top of the degassing porphyry. Magmatic gases were absorbed at shallow levels in the crust and interacted with ground waters (Giggenbach, 1992, Hedenquist & Lowenstem, 1994). The resulting acidic and oxidizing solutions
promote the wholesale destruction of the rock and production of highly leached silica residue and quartz-alunite alteration. With regards to the source of the metals in this highly acidic environment, Hedenquist (1995) suggests that metal-fluxes solely in the magmatic gases are not high enough to produce ore deposits, because these fluids are not capable of transporting metals in sufficient amounts assuming a realistic time span for degassing of the magma. Also, Hedenquist et al. (1999, 1995) and Arribas et al. (1995) suggest that the acidic fluid alone is not responsible for ore formation, rather they surmise that ore components originated from the magmatic fluids and the altered rock.

Hedenquist’s (1999, 1995) idea supports mixing of magmatic fluids with ground waters to produce fluids that can transport ore in sufficient amounts. Metals may thus be derived from surrounding crust. This Re-Os evidence supports the notion that the surrounding crust could have contributed a large portion of the metals in the district. The initial $^{187}\text{Os} / ^{188}\text{Os}$ ratio of 1.18 contains a large portion of radiogenic (crustal) Os considering the present day mantle value is around 0.13 (Meisel et al, 1996). In fact, the concentration of both elements and the initial $^{187}\text{Os} / ^{188}\text{Os}$ measured in the high-sulphidation sulfides reflects the average values of the continental crust determined by Turekian (1993). Therefore, the metamorphosed crustal rocks (mostly sedimentary rocks) of the Santander massif into which the porphyry intruded could have been a major source for the Os and by inference gold present in the high-sulfidation California deposit.

However, the data do not preclude the possibility that the porphyry was responsible for all of the metals present. Recent Re-Os work on porphyry copper systems (Mathur et al., 2000) reveals that the lower crust, or even the subducting slab could be radiogenic sources for metals in these systems. Therefore, acquisition of this radiogenic value by the magmatic system could be a reflection of either metals inherited in mantle wedge- lower crustal domain where the magma started, or metals leached from the surrounding crust.

3. The low-sulfidation Vetas deposit is distinctly different from the California high-sulfidation system. This could reflect differences in the behavior of Re-Os due to
changing composition of the mineralizing fluid, or the mineralization of the Vetas deposit is completely unrelated to the California porphyry.

The Vetas low-sulfidation deposit formed 10 km away from the California dacite porphyry. The alteration mineralogy implies that mineralizing fluids had a near neutral-pH that may have been derived from a mixture of magmatic and meteoric fluids that were neutralized during reaction with wall rocks (Hedenquist, 1986, Heald, 1987). The Re-Os data from the Vetas deposit indicates that the age or source of mineralization is different to the California high-sulfidation deposit. The Re-Os isotopes system appears not to be in isotopic equilibrium with the Vetas system.

There are two possible geochemical explanations for this behavior: the Vetas system was in equilibrium with respect to Re-Os, but a subsequent geologic event disturbed the system, or the initial mineralizing event never reached complete equilibrium with respect to Re-Os isotopes. There is no geologic evidence that supports the first possibility. For instance, no overprinting characteristics, such as relics of high-sulfidation minerals or similar element abundance as seen in the high-sulfidation California system, exists in the Vetas deposit. The second scenario appears more reasonable. Perhaps the lower temperature, pH, and oxidizing (dominated by a meteoric component) fluids associated with the Vetas system did not achieve complete equilibrium with respect to Re-Os isotopes. The disequilibrium coupled with the higher Re concentrations of the Vetas system could represent greater leaching and acquisition of surrounding crustal metals. Thus, the porphyry could be seen as a heat engine that drove circulating meteoric groundwaters that leached Re, Os and other metals from the crust and redeposits them in economic concentrations.

Hedenquist and Gulson (1992) examined the Pb isotopic composition of modern epithermal systems in the Taupo volcanic field. Their results indicate two distinct Pb ore domains: one in which the sulfide Pb isotopic composition matched the associated andesitic volcanism, and another set of heterogeneous Pb values. The data lead them to conclude that the homogenous set of samples involved a process that has a magmatic component, whereas the heterogeneous samples represented a process that is dominated
by leaching of basement rocks. The Re-Os data of the California and Vetas systems could be representing an ancient analog to what was seen in the Taupo volcanic field. The isochron of the high-sulfidation system represents the equilibrium achieved by the system with the magmatic component, and the disequilibrium and greater concentrations of Re in the low-sulfidation system reflect the leaching of the surrounding crust.

Acknowledgements

The authors would like to thank the CDMB, the “Compañía del Acueducto Metropolitano de Bucaramanga E.S.P.”, the “Ministerio de Minas y Energía“ and the “Gobernación de Santander“ for cooperation during the sampling process. Analytical work was supported by the National Science Foundation Grants EAR 9708361, and EAR 9628150, and a instrumentation grant from the W. M. Keck Foundation.

References


Table 4.1 - Re- Os concentrations and isotopic ratios. Error calculation is described in the text and Mathur et al (2000), and errors are provided for the California samples that make and isochron.

<table>
<thead>
<tr>
<th>sample</th>
<th>Re (ppt)</th>
<th>Os (ppt)</th>
<th>$^{187}$Re/$^{188}$Os</th>
<th>$^{188}$Os/$^{186}$Os</th>
</tr>
</thead>
<tbody>
<tr>
<td>California-1</td>
<td>6716</td>
<td>32</td>
<td>1299 ± 103</td>
<td>2.42 ± 0.07</td>
</tr>
<tr>
<td>California-1</td>
<td>4436</td>
<td>30</td>
<td>917 ± 73</td>
<td>2.08 ± 0.04</td>
</tr>
<tr>
<td>California-2</td>
<td>33405</td>
<td>33</td>
<td>7187 ± 718</td>
<td>8.48 ± 0.42</td>
</tr>
<tr>
<td>California-2</td>
<td>803</td>
<td>19</td>
<td>244 ± 20</td>
<td>1.51 ± 0.07</td>
</tr>
<tr>
<td>California-2</td>
<td>4447</td>
<td>34</td>
<td>668 ± 50</td>
<td>1.78 ± 0.03</td>
</tr>
<tr>
<td>Vetas-1</td>
<td>129213</td>
<td>29</td>
<td>41874</td>
<td>7.54</td>
</tr>
<tr>
<td>Vetas-2</td>
<td>153479</td>
<td>27</td>
<td>56136</td>
<td>8.11</td>
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<td>43570</td>
<td>30</td>
<td>8651</td>
<td>1.85</td>
</tr>
</tbody>
</table>
Figure 4.1 - Location map for the Santender Massif. Dark Circles indicate the mine locations and the darkened box indicate city location.
Figure 4.2- Geologic cross section of the area illustrating the complex stratigraphic relationships of the area.
Figure 4.3- Isochron plot of the data. None of the low sulfidation Vetas samples fall on the high sulfidation California isochron, or form any trend with age significance.
Chapter 5- Relationship between copper tonnage of Chilean base-metal porphyry deposits and Os isotope ratios

Abstract

Re-Os isotopes in pyrite and chalcopyrite from early high-temperature hypogene alteration assemblages in Chilean porphyry copper deposits identify the source of Os and, by inference, Cu in these ore systems. Typical concentrations for Os in both pyrite and chalcopyrite are between 7 and 30 parts per trillion (10^{-12} grams per gram), and for Re between 0.200 to 10 parts per billion (10^{-9} grams per gram). Re-Os isochrons yield ages, and initial $^{187}$Os/$^{188}$Os ratios for the sulfides. The isotopic data reflect the relative contributions of copper from the mantle and crust in Chilean porphyry copper deposits. Seven ore deposits that reside in different tectonic terranes and represent distinct epochs of mineralization in Chile were studied. The initial osmium ratios of the first stage of mineralization 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. 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. Keywords: Porphyry Copper, Re-Os, Chile

Introduction

Because of its chalcophile and siderophile nature, the Re-Os isotope system has long been recognized as a possible geochemical tool for tracing the origin of metals and directly dating mineralization (Luck and Allegre, 1980; McCandless and Ruiz, 1993; Frei et al. 1998; McInnes et al., 1999). This is in contrast to most other radiogenic isotopic systems, which typically consist of lithophile elements that concentrate in associated
alteration silicates rather than sulfides. Furthermore, because Re is highly incompatible in the mantle compared to Os, the Re/Os ratio of the crust is highly enriched compared to that in the mantle (Drake and Jones, 1983; Fleet and Stone, 1991; Fleet et al., 1999). The time-integrated consequence of this elemental behavior is that the crust evolves towards elevated $^{187}\text{Os}/^{188}\text{Os}$ ratios in comparison to the chondritic mantle, which is approximately 0.13 today (Morgan et al., 1995; Shen et al., 1996).

In this study, Os isotope ratios are used to trace the relative importance of the crust and mantle as sources of Os in the porphyry copper deposits of Chile. Due to the chalcophile nature of this element, the sources of Os may be used as proxy for the sources of Cu.

Porphyry copper deposits, which are major geochemical anomalies of the Earth's crust, are characterized by large concentrations of chalcophile elements. Their occurrence is linked to the intrusion of subduction-related magmas at shallow levels of the crust (e.g. Sawkins, 1990). Subsequent development of large hydrothermal systems (Titley and Hendrick, 1978; Lang and Titley, 1998) around the intrusions deposited Cu-bearing minerals in stockwork fractures. There are many theories on the reason why these deposits form (Clark, 1993; Williams, 1994). The possible controls for mineralization include regional structures, a specific chemical and/or physical evolution of the magmatic and hydrothermal system, and the sources and availability of sulfur and/or the ore-forming metals. Some studies have suggested the size of base-metal porphyry deposits may be related to mantle processes, and that the larger deposits should have a significant mantle signature (Clark, 1993; McInnes et al., 1999). This study tests this hypothesis and centers on using Os isotopes to decipher the source of ore-forming metals.

**Geologic Background**

Chile is the leading copper producer in the world and has some of the largest base-metal porphyry deposits known. The ore deposits formed in large hydrothermal systems during Cenozoic continental arc magmatism (Ramos, 1989). The ore-bearing porphyries intrude a collage of igneous, sedimentary and metamorphic rocks that were
accreted to the margin of South America from the late Proterozoic through the Cretaceous (Ramos, 1989; Richards, 1995). The suite of porphyry copper deposits chosen for this study spans three distinct intervals of magmatic activity: 60, 40-30 and 10-4 Ma (Sillitoe, 1988). These deposits have been reviewed in detail (Zentilli, 1974; Gustafson and Hunt, 1975; Alpers and Brimhall, 1988; Sillitoe, 1988, 1990; Skewes and Stern, 1994; Williams, 1994).

The plutonic rocks associated with copper mineralization range in composition from diorite to quartz monzonite. The deposits are characterized by a core of hypogene alteration (which includes the assemblages of biotite-orthoclase, and quartz-sericite) and mineralization with chalcopyrite, bornite and sometimes molybdenite, as the minerals that host the economic elements of interest. It is generally thought that the early sulfides in these deposits are precipitated from dominantly magmatic fluids accompanying the intrusion. Later sulfides precipitate from meteoric waters that invade the system as it cools (e.g. Beane and Titley, 1981; Guilbert, 1986; Beane and Bodnar, 1995). Low-temperature supergene processes that are not related to the primary magmatic-hydrothermal system redistribute the economically important minerals making these deposits economically viable, but presumably do not add more ore-forming elements to the system.

The ultimate source of the base metals (i.e. copper and molybdenum) could either be magmatic-with crustal or subcrustal components, or hydrothermal- through leaching of the surrounding host-rocks (Sillitoe, 1988). Previous studies in this part of the Andean Cordillera yielded conflicting results on this issue. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, rare earth element, and trace element data from the intrusive rocks indicate that the magmas associated with the mineralization were derived from the mantle, and interacted very little with crustal rocks (Gustafson and Hunt, 1975; Shibata et. al., 1984; Munizaga et. al., 1985, Stern and Skewes, 1996). Pb isotopes, however, indicate a more complex source for Pb, that also includes the crust (Puig et al., 1988; MacFarlane et al., 1990; Tosdal, 1995).
Analytical Techniques

The sulfide samples analyzed for this study are associated with the early high temperature alteration silicates of either orthoclase-biotite assemblages or quartz-sericite (Table 5.1). The samples were wrapped in paper and crushed with a hammer in an effort to minimize contamination with platinum group elements. After selection of pure sulfide grains from the crushed rubble, the samples were sieved and hand-picked until enough clean sulfides were obtained. Typically, 0.8-1.5 grams of sample was dissolved in a Carius tube in 4:1 HNO₃-HCl acid mixture. H₂O₂ was added to the acid mixture to ensure complete oxidation of the samples and spike equilibration (Shirey and Walker, 1995). Os was separated and purified in a two-stage distillation process similar to that described by Frei et. al. (1998). Rhenium was extracted and purified through column chemistry. The isotopic measurements were made by negative thermal ionization mass spectrometry (Creaser et. al., 1991).

Internal reproducibility for the measurements is always better than 0.2% (2σ), however this value underestimates the error of the analysis because of variable contribution of Os from the procedural blanks. Whole procedure chemical blanks during this study varied from 1.5 to 2.6 picograms for Os and 25 to 35 picograms for Re. Since the greatest source of error in these low concentration analyses is the variable contribution of the Os blank, errors for both the $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ are calculated by varying the concentration of the Os blank ($^{187}\text{Os}/^{188}\text{Os}$ for the blank = 0.18) between 1.5 and 2.6 pg for Os. The calculated errors are listed in Table 1 as percent deviation on the mean. Age and initial $^{187}\text{Os}/^{188}\text{Os}$ ratios were calculated with the program MACDAT-2, written by Clark Isachsen and Drew Coleman using the algorithms of York (1969).

Re-Os Results

Typically the Os concentrations for pyrite and chalcopyrite range between 7-30 ppt, except for the samples from Quebrada Blanca, which contain 230 ppt. The Re concentrations for all the samples analyzed range from 150 ppt to 20 ppb (Table 5.1). Large variations in the Re/Os ratios of the sulfides from base-metal porphyry deposits (Table 5.1), often yield isochrons from single hand samples. Presumably, small platinum
group element rich inclusions control in the distribution of Re-Os in sulfides, and record the Os isotopic characteristics at the hand sample scale.

Seemingly, Os is derived from the associated intrusion in each of the deposits since early fluids are thought to be principally magmatic. The source of the Os may change through time as the hydrothermal system evolves from one dominated by magmatic to meteoric waters. For example, Ruiz et al. (1997) and Freydier et al. (1997) show that the expected changes in the source of the Os for El Teniente could be documented with well-constrained samples.

The initial Os ratios for the deposits studied here were obtained from isochrons when possible. El Salvador (Fig. 5.1a) yields an isochron with the expected age (Gustafson and Hunt, 1975) and initial Os ratio. Samples associated with orthoclase-biotite, and samples associated with quartz-sericite alteration assemblages lie on a similar isochron. The Re/Os ratios of the samples associated with quartz-sericite are more radiogenic than those of the samples associated with orthoclase-biotite, suggesting Re mobility early in the history of the deposit. The Re mobility, however, must have occurred within the error of the age of the isochron. Chuquicamata yields an isochron (Fig. 5.1b) from paragenetically late sulfides that correlates with the youngest Ar ages reported (ca. 31 Ma, Reynolds et al., 1998). Two samples from a paragenetically earlier mineralizing event (35 Ma) yield an initial ratio that is less radiogenic than the late mineralization. Cerro Colorado samples form an errorchron with a reasonable age, but high error on the age and initial isotopic ratio. The initial $^{187}$Os/$^{188}$Os ratios that are reported in Table 1 include a conservative view of their error as already discussed.

Discussion

A central question in metallogenesis is what controls the size of ore deposits. This question has been difficult to address because the variables that may control total tonnage of the ore metals are many and intertwined. Here we use Os isotopes to constrain one of the possible controls – the source of the ore-forming metals. Possible sources for the Os, and by inference Cu, are the mantle wedge, the subducting slab and accompanying sediments, and the diverse reservoirs in the upper and lower continental
crust (e.g. Esser and Turekian, 1993; Brandon, 1996; Chesley and Ruiz, 1999; Saal et. al. 1998).

Figure 5.2 shows a correlation between the initial \(^{187}\text{Os}/^{188}\text{Os}\) ratio of base metal porphyry deposits of Chile and their copper content. The copper tonnage for the deposits was obtained from Long (1995). The analytical errors of the Os isotopic values have already been addressed and we believe are conservative. The error on the tonnage is difficult to evaluate. Although the calculation for absolute copper content is based on economic assumptions and may change, it is unlikely that the values would change the order of the deposits. The correlation shows that the largest deposits – Chuquicamata and El Teniente – have the lowest initial \(^{187}\text{Os}/^{188}\text{Os}\) ratios. These low Os ratios (~ 0.15) are nevertheless more radiogenic than those expected for the mantle beneath continental arcs (0.13-0.15; Brandon et. al., 1996), and indicate that the crust – probably the lower crust – (e.g. Chesley and Ruiz, 1998) contributes Os to the magmatic processes that produce base-metal porphyry deposits. The smaller deposits have \(^{187}\text{Os}/^{188}\text{Os}\) ratios that are very radiogenic (~ 5). These highly radiogenic values require a significant contribution of crustal Os to the magmatic and hydrothermal system.

The Os isotope data plotted in Figure 5.2 do not correlate with the age of the basement that underlies the deposits. This indicates that the size of the deposits and the source of the Os are independent of the age of the basement. For example, the deposits in northern Chile – i.e., Cerro Colorado –, are in the Arequipa terrane, which has a Proterozoic basement, whereas El Teniente is on the Chilenia terrane, which is floored by Ordovician metamorphic rocks. Tosdal (1995) suggested that differences in metal budgets for ore deposits between lat. 26° and 28°S are linked to the influence of crustal assimilation. Magmas that contain large amounts of crustal components may be diluted of base metals as the magmas slowly ascend to the surface and extensively interact with the crust. This could be a possible geochemical explanation for the observed regional trend of copper versus Os initial ratios.

Initial Os ratios within ore deposits also illustrate the isotopically complex nature of the fluids that are involved in mineralization. The isochrons in Figure 5.1 from
Chuquicamata and El Salvador show how the sources of metals associated with different hypogene alteration events within an ore deposit can remain relatively similar or change drastically. For instance, in Chuquicamata, pyrite associated with quartz-sericite from the later (31 Ma) alteration events have initial $^{187}\text{Os} / ^{188}\text{Os}$ of $\sim 1$, whereas chalcopyrite from an earlier system (35 Ma) associated with biotite-orthoclase alteration have an Os initial of 0.15. Thus, the second mineralization event has a more significant crustal signature, than the earlier event. El Salvador presents a different case in which the orthoclase-biotite and quartz-sericite alteration was produced by one event. Pyrite and chalcopyrite associated with both orthoclase-biotite and quartz-sericite alteration lie on the same isochron. In this case, the sources of metals for both alteration and mineralization events have approximately similar sources. These two deposits demonstrate the need to thoroughly understand the age constraints of the mineralization and events within an ore deposit in order to interpret the isotope results.

There is a relationship between age and initial ratio of the earliest mineralization for the mid-Tertiary base-metal porphyry deposits. The oldest Re-Os age for this group of deposits is from Quebrada Blanca, which yields an age of $45 \pm 3$ Ma. This age is slightly older than the 38 Ma K-Ar age reported by Hunt et al. (1983). The initial Os ratio of this deposit is $1.28 \pm 0.06$, which is the most radiogenic value for the mid-Tertiary base-metal porphyry deposits of central-northern Chile. The youngest deposit in this area of Chile is Chuquicamata, which is 35 Ma (Reynolds, et al., 1998). Chuquicamata has an Os initial ratio of 0.15. Figure 5.3 illustrates the trend and shows a strong correlation between age of mineralization and Os isotopic ratio. The trend toward more primitive initial Os ratios with time suggests that regional structural processes may have allowed later mantle-derived magmas to rise without as much interaction with the crust in comparison to the earlier magmas.

Summary

Re-Os isotope measurements of pyrite and chalcopyrite samples from porphyry deposits of Chile show a correlation between total copper tonnage and initial $^{187}\text{Os} / ^{188}\text{Os}$ ratios. All the Os isotope ratios are more radiogenic than those expected for purely
mantle-derived magmas. However, the larger deposits have the least radiogenic Os initial ratios, indicating the least amount of crustal Os.

The good correspondence between size of the deposit and Os isotope systematics has important academic and economic consequences. The data show that the most significant source of the metals is in the mantle or lower crust and that dilution by filtering of magma through higher crustal rocks makes the deposit smaller. The correlation developed here may be a useful exploration tool in that Os isotope measurements may give an indication of the potential size of the deposit.

Acknowledgments

We thank Mark Baker for all his help in the laboratory, Miguel Tapia, Eduardo Fernandez, Esteban Acuña from Rio Algom mining Company, Roberto Blondel, Walter Orquera, El Salvador CODELCO and Roberto Freraut and Jose Rojas from Chuquicamata CODELCO who assisted in collecting the samples and provided relevant information about the ore deposits. BHP and Phelps-Dodge kindly allowed us access to their mines and logistic support while sampling. The work was also supported by NSF through grants EAR 9708361, and EAR 9628150 and FONDECYT through grant 1970403. We thank Spencer Titley, De Verle Harris, John Chesley, Fernando Barra, Hugh Rollinson, and an anonymous reviewer for their constructive comments on earlier drafts of this paper.

References


Reynolds, P., Ravenhurst, C., Zentilli, M., Lindsay, D. (1998) High precision \(^{40}\text{Ar}/^{39}\text{Ar}\) dating of two consecutive hydrothermal events in the Chuquicamata porphyry copper system, Chile. Chemical Geology, 148, 45-60.


# Table 5.1. Re-Os results for Porphyry Copper Deposits

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Phases</th>
<th>Re</th>
<th>Os</th>
<th>(^{187})Re/(^{188})Os</th>
<th>Dev.*</th>
<th>(^{187})Os/(^{188})Os</th>
<th>Dev.*</th>
<th>Initial Os Ratio</th>
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<td>Quebrada Blanca</td>
<td>Py.(^1)</td>
<td>32000</td>
<td>19</td>
<td>94730</td>
<td>10</td>
<td>72.46</td>
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<td>21488</td>
<td>238</td>
<td>521</td>
<td>4</td>
<td>1.66</td>
<td>3</td>
<td>1.23±/-0.07</td>
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<tr>
<td>Quebrada Blanca</td>
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<td>21000</td>
<td>244</td>
<td>499</td>
<td>4</td>
<td>1.67</td>
<td>4</td>
<td>1.23±/-0.08</td>
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<tr>
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<td>Py.(^1)</td>
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<td>24</td>
<td>138</td>
<td>3</td>
<td>1.08</td>
<td>2</td>
<td>1.01±/-0.014</td>
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<tr>
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<td>7918</td>
<td>6</td>
<td>15097</td>
<td>14</td>
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<td>5</td>
<td>1.01±/-0.014</td>
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<tr>
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<td>5854</td>
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<td>17</td>
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<td>0.21</td>
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<tr>
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<td>9</td>
<td>15110</td>
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<td>8632</td>
<td>6</td>
<td>18366</td>
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<td>23396</td>
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<tr>
<td>ELS6687mix Ch. + py(^2)</td>
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<td>6</td>
<td>10493</td>
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<td>8.19</td>
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<tr>
<td>ELS6687mix Ch. + py(^2)</td>
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<td>3548</td>
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<td>ELS6687cpy Ch.(^2)</td>
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<td>7178</td>
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<td>7</td>
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<td>Cerro Colorado</td>
<td>Py.(^1)</td>
<td>883</td>
<td>13</td>
<td>1202</td>
<td>37</td>
<td>9.9</td>
<td>29</td>
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<td>13</td>
<td>1280</td>
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<tr>
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<td>23</td>
<td>120921</td>
<td>15</td>
<td>90.2</td>
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<td>Py.(^2)</td>
<td>8076</td>
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<td>3455</td>
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<td>Agua Rica</td>
<td>Ch.(^2)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>20.02</td>
<td>3</td>
<td>---</td>
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<td>2063</td>
<td>19</td>
<td>4.85</td>
<td>10</td>
<td>-4.68(^1)</td>
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</table>

Note: Ch.—chalcopyrite, py.—pyrite, 1 =quartz-sericite 2= biotite-orthoclase

* Dev.—percent deviation; calculated by changing the concentrations of the blank.
† Value calculated by age correcting Re/Os ratios.
Figure 5.1 - isochron plots a) El Salvador pyrite and chalcopyrite isochron with an age of 39 +/- 2 Ma, MSWD 0.79. b) Chuquicamata pyrite from quartz-sericite alteration isochron with an age of 31 +/- 2, MSWD 1.0. Two samples of chalcopyrite from orthoclase-biotite alteration suggest an age of about 33 Ma.
Figure 5.2- Data from El Teniente (Ruiz et al., 1997). Y-axis is variable depending on the economy (Long, 1995) and technological advances; nevertheless relative size comparisons between deposits remain constant. Agua Rica from Argentina is also included in plot.
Figure 5.3 - Timing of mineralization in porphyries of central Chile against initial Os. Note that initial Os isotope ratio of only first mineralization.
Chapter 6- Conclusions

There are several important general observations and conclusions that can be drawn from this study, and they can be seen on three levels as discussed in the introduction. Appendix E provides more data for the deposits studied in chapters 2-5 and also data from other deposits. Table E.1 summarizes these results, and data treatment is discussed extensively in Chapters 3 and 5.

1. The results of the study show that on the average, sulfides and magnetite from typical stockwork mineralization, which can be hydrothermal or magmatic in these systems contain 7-30 ppt Os and 1-20 ppb Re. The initial $^{187}\text{Os} / ^{188}\text{Os}$ values for these minerals range from 0.15-50.

2. There is a crustal component in all of the sulfides from the ore deposits analyzed regardless of the arc environment. The source for the radiogenic Os component may include the metasomatized mantle from which the magma originated, to the crustal rocks into which the magma intersected. Figure 6.1 illustrates this observation because all deposits lie above the present chondritic mantle value.

3. There is a correspondence between the initial $^{187}\text{Os} / ^{188}\text{Os}$ versus copper content for the Andean Porphyry copper deposits. Addition of Escondida, Toquepala, Cuajone, and Spence to this relationship developed in chapter 5 illustrates a relatively cohesive correspondence. The new data are plotted in fig. 6.2 and were obtained after chapter 5 was published, and fall on the curve presented in this *Geology* article. The smaller deposits in the Peruvian Andes, and Spence have very radiogenic signatures compared to
the larger deposits in Chile. As stated in chapter 5, this regional relationship could reflect that the most significant source of the copper is in the mantle or lower crust.

4. The correlation between initial $^{187}\text{Os}/^{188}\text{Os}$ ratios and copper tonnage is not global. Figure 6.3 is a plot of the deposits analyzed and it illustrates that there is no correlation between the size of the Chilean and South Pacific ore bodies analyzed. Panguna has a distinct mantle signature, but does not contain nearly the amount of copper present in the gigantic deposits of the Andean Cordillera. Also plotted is the Candelaria district, and this result clearly lies off of the trend of the porphyries of the Chilean Cordillera. As described in chapter 2, however, this ore body may not be a typical porphyry copper.

5. The Os data suggest that gold in porphyry systems can originate from sedimentary rocks. Re-Os results from gold rich ores of Grasberg, Nickel Plate, and Bucaramanga indicate that sedimentary rocks most likely contribute a large portion of metals to the porphyry systems. Figure 6.4 illustrates this point.

6. Re-Os concentrations present in the ore styles analyzed here are diverse and end member concentrations are difficult to establish for specific deposit types. Figure 6.5 is a concentration plot of all the Re-Os data from this thesis and the literature. A majority of the fields overlap, however Cu-Au or just Au systems have elevated concentrations of Re and Os in comparison to Cu-Mo systems. Candelaria Fe rich Cu-Au mineralization has higher concentrations of Os and less Re then typical Chilean Cu-Mo Porphyries. These apparent differences could be linked to variety of processes responsible for metallogenesis during arc magmatism.
Figure 6.1- Illustration of the crustal signature in the deposits analyzed, arrows indicate initial values greater than 1.5
Figure 6.2 - Log plot of Os versus Cu content in Andean Copper Deposits

- Red diamonds: Chilean Porphyry Copper Deposits
- Blue diamonds: Peruvian Porphyry Copper Deposits
Figure 6.3- Log plot of Os versus Cu content in all copper deposits studied.
Figure 6.4- Crustal sources for Au in porphyry environments
Figure 6.5- Concentration of Re and Os for various Ore Deposits
Appendix A: Sample descriptions

In the following spreadsheet there are sample names, locations, and descriptions for all of the samples used for the study. Each sample originated from a different part of the ore body. Specific rock units from which the samples were obtained are included in the alteration section of the data table. The sample numbers for certain samples pertain to the specific drill core from which the sample originated. Abbreviations are explained on the last page of the section.
<table>
<thead>
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<th>Mine</th>
<th>Sample Name</th>
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<th>Phases present</th>
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<td>Chuquicamata, Chile</td>
<td>Chuqui-2</td>
<td>propylitic</td>
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<td>cpy- big piece with cc dust</td>
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<td>qtz-ser destroyed</td>
<td>sphalerite</td>
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<td>qtz-ser</td>
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<td>Chuqui</td>
<td>rock</td>
<td>Elina granite and metasediments</td>
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<td>Tourmaline breccia</td>
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<tr>
<td>El Salvador, Chile</td>
<td>1104-515</td>
<td>C.Antiqua, qtz-ser</td>
<td>py +cpy</td>
</tr>
<tr>
<td>El Salvador, Chile</td>
<td>1104-565</td>
<td>C.Antiqua, qtz-ser</td>
<td>py +cpy</td>
</tr>
<tr>
<td>El Salvador, Chile</td>
<td>1104-575</td>
<td>C.Antiqua, qtz-ser</td>
<td>py</td>
</tr>
<tr>
<td>Antapaccay, Peru</td>
<td>Antap- moly</td>
<td>BHP Prospect, PCD</td>
<td></td>
</tr>
<tr>
<td>Quebrada Blanca, Chile</td>
<td>QB-2</td>
<td>Qtz. Monzon. Breccia</td>
<td>cpy +py</td>
</tr>
<tr>
<td>El Salvador, Chile</td>
<td>549-152</td>
<td>Q. M, chl-prop</td>
<td>py</td>
</tr>
<tr>
<td>El Salvador, Chile</td>
<td>6707-128</td>
<td>Q.Granio, supergene</td>
<td>cc+ cpy +py</td>
</tr>
<tr>
<td>El Salvador, Chile</td>
<td>6744-1</td>
<td>Q. Granito, supergene</td>
<td>cc+brn+cpy</td>
</tr>
<tr>
<td>Collahuasi, Chile</td>
<td>Coya-4</td>
<td>Unity porphyry k-spar</td>
<td>cpy+ py</td>
</tr>
<tr>
<td>Collahuasi, Chile</td>
<td>Coya-6</td>
<td>Rosario, qtz-ser</td>
<td>cpy +py</td>
</tr>
<tr>
<td>Collahuasi, Chile</td>
<td>Coya-2</td>
<td>Rosarios, transitional Mo vein</td>
<td>Moly</td>
</tr>
<tr>
<td>Mine</td>
<td>Sample Name</td>
<td>Alteration</td>
<td>Phases present</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-------------</td>
<td>-----------------------------------------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>Pelambres, Chile</td>
<td>Pel-1</td>
<td>thick quartz +moly vein</td>
<td>Moly, crystalline thick vein</td>
</tr>
<tr>
<td>Pelambres, Chile</td>
<td>Pel-2</td>
<td>qtz-ser from micro diorite</td>
<td>py</td>
</tr>
<tr>
<td>Pelambres, Chile</td>
<td>Pel-3</td>
<td>qtz-ser from micro diorite</td>
<td>py</td>
</tr>
<tr>
<td>Pelambres, Chile</td>
<td>Pel-4</td>
<td>cpy from mafic breccias</td>
<td>py +cpy in Au and Mo breccia</td>
</tr>
<tr>
<td>Escondida, Chile</td>
<td>escex3-1</td>
<td>qtz-ser fine grained ser</td>
<td>fine grained py</td>
</tr>
<tr>
<td>Escondida, Chile</td>
<td>esc2700ser</td>
<td>qtz-ser fine grained ser</td>
<td>fine grained py</td>
</tr>
<tr>
<td>Escondida, Chile</td>
<td>escex1-2</td>
<td>qtz-ser fine grained ser</td>
<td>fine grained py</td>
</tr>
<tr>
<td>Escondida, Chile</td>
<td>esc11150arg</td>
<td>argillic over print, +Kaol.</td>
<td>fine grained py</td>
</tr>
<tr>
<td>Escondida, Chile</td>
<td>esc2755arg</td>
<td>argillic over print, +Kaol.</td>
<td>fine grained py</td>
</tr>
<tr>
<td>Escondida, Chile</td>
<td>Esc-1</td>
<td>from 1st pulse of mag</td>
<td>magnetite from diorite</td>
</tr>
<tr>
<td>Escondida, Chile</td>
<td>Esc-2</td>
<td>from main min. intrusion</td>
<td>magnetite from diorite</td>
</tr>
<tr>
<td>Escondida, Chile</td>
<td>Esc-hydro</td>
<td>hydrothermal magnetite</td>
<td>thick vein of magnetite</td>
</tr>
<tr>
<td>Copequaire, Chile</td>
<td>Cops-2</td>
<td>Mo from qtz. Envelope</td>
<td>fine grained moly</td>
</tr>
<tr>
<td>Escalonnes, Chile</td>
<td>ELN-1</td>
<td>gross. Grt</td>
<td>thick chalcopyrite veins</td>
</tr>
<tr>
<td>Panguna, Boug. P.N.G.</td>
<td>panguna</td>
<td>late stage brn. Cc. coat</td>
<td>bornite on qtz vein with calcocite</td>
</tr>
<tr>
<td>Panguna, Boug. P.N.G.</td>
<td>103031</td>
<td>late stage vein</td>
<td>massive cpy vein</td>
</tr>
<tr>
<td>Panguna, Boug. P.N.G.</td>
<td>panguna 102598</td>
<td>Qtz-cpy, leuco. Qtz-diorite</td>
<td>fine grained brown sph</td>
</tr>
<tr>
<td>Demberkoy, Turkey</td>
<td>Dem-1</td>
<td>late stage vein</td>
<td>Thick vein of py</td>
</tr>
<tr>
<td>Panguna, Boug. P.N.G.</td>
<td>panguna 103017</td>
<td>Qtz-ser, from qtz. Monz.</td>
<td>crystalline py</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>GSP cov+py*</td>
<td>qtz-ser, Leuco. Qtz-diorite</td>
<td>grainy py coated with cov.</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>KL4-40</td>
<td>late cov. +py event</td>
<td>vein of py</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>high sulfidation</td>
<td>mineralized vein sed.</td>
<td>py</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>grs37194</td>
<td>Massive Sulfide</td>
<td>py</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>Ki40-05high</td>
<td>Massive sulfide</td>
<td>py +cpy</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>hszx22</td>
<td>border of massive sulfide</td>
<td>py</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>grs194cpy</td>
<td>massive sulfide?</td>
<td>py</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>cpy pure</td>
<td>from concentrate</td>
<td>massive mag. With large cpy veins</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>Moly-1</td>
<td>from silicified vein</td>
<td>fine grained concentrate</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>MGI cpy</td>
<td>massive cpy vein</td>
<td>fine grained crystalline molybdenite</td>
</tr>
<tr>
<td>Grasberg, Indonesia</td>
<td>Au</td>
<td>Gold Concentrate</td>
<td>grab sample from pit in MGI</td>
</tr>
<tr>
<td>Cuijone, Peru</td>
<td>95729</td>
<td>thick mo vein</td>
<td>Gold</td>
</tr>
<tr>
<td>Cuijone, Peru</td>
<td>95728</td>
<td>qtz-ser from rhyolite</td>
<td>cross-cuts oldest basaltic anodesite</td>
</tr>
<tr>
<td>Cuijone, Peru</td>
<td>95731</td>
<td>Pb Zn rich dike</td>
<td>cpy +py</td>
</tr>
<tr>
<td>Toquepala, Peru</td>
<td>95719</td>
<td>Mo from qtz-ser</td>
<td>sph. +gal</td>
</tr>
<tr>
<td>Toquepala, Peru</td>
<td>95720</td>
<td>gyp +anhydrite</td>
<td>crystalline mo</td>
</tr>
<tr>
<td>Cerro Verde, Peru</td>
<td>95734</td>
<td>mo from transitional vein</td>
<td>purple anhydrite with chalcopyrite</td>
</tr>
<tr>
<td>Bucaramanga, Columbia</td>
<td>California-1</td>
<td>gravity separate, high sulf.</td>
<td>did magnetitic separate</td>
</tr>
<tr>
<td>Bucaramanga, Columbia</td>
<td>California-2</td>
<td>gravity separate, high sulf.</td>
<td>did magnetitic separate</td>
</tr>
<tr>
<td>Bucaramanga, Columbia</td>
<td>Vetas-1</td>
<td>gravity separate, low sulf.</td>
<td>did magnetitic separate</td>
</tr>
<tr>
<td>Bucaramanga, Columbia</td>
<td>Vetas-2</td>
<td>gravity separate, low sulf.</td>
<td>did magnetitic separate</td>
</tr>
<tr>
<td>Nickel Plate, B.C.</td>
<td>Ni-plate-1</td>
<td>chl+diop.+alman grt.</td>
<td>arsenopyrite</td>
</tr>
<tr>
<td>Nickel Plate, B.C.</td>
<td>Canton-1</td>
<td>chl+diop.+alman grt.</td>
<td>pyrohottite</td>
</tr>
<tr>
<td>Nickel Plate, B.C.</td>
<td>Canton-2</td>
<td>chl+diop.+alman grt.</td>
<td>arsenopyrite</td>
</tr>
</tbody>
</table>

Table 1 contains sample information. py = pyrite, moly = molybdenite, cpy = chalcopyrite, mag. = magnetite, sph = sphalerite, gal. = galena, chl = chlorite, diop. = diopside, alman grt = almandine garnet, gyp. = gypsum, qtz. = quartz, ser. = sericite, k-spar = potassium felspar, bio. = biotite.
Appendix B

Molybdenite Ages:

All of the molybdenite ages for porphyry copper and related mineralization are reported in table 1. All errors for molybdenite data consider the error associated with the calculated concentration of the Re spike. The errors of the ages would greatly decrease if instrument error was only considered.
<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Location</th>
<th>Re (ppm)</th>
<th>$^{187}$Os (ppb)</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Candelaria moly-1</td>
<td>Chile</td>
<td>77</td>
<td>22.35</td>
<td>114.3 +/- 0.6</td>
</tr>
<tr>
<td>Candelaria moly-1</td>
<td>Chile</td>
<td>73</td>
<td>22.06</td>
<td>115.1 +/- 0.6</td>
</tr>
<tr>
<td>Collhuasi</td>
<td>Chile</td>
<td>447</td>
<td>13.78</td>
<td>33.4 +/- 0.1</td>
</tr>
<tr>
<td>Copaquirre</td>
<td>Chile</td>
<td>81</td>
<td>3.98</td>
<td>38.3 +/- 0.1</td>
</tr>
<tr>
<td>Copaquirre</td>
<td>Chile</td>
<td>85</td>
<td>4.59</td>
<td>37.2 +/- 0.2</td>
</tr>
<tr>
<td>Escondida</td>
<td>Chile</td>
<td>1355</td>
<td>17.15</td>
<td>33.7 +/- 0.16</td>
</tr>
<tr>
<td>Pelambres</td>
<td>Chile</td>
<td>835</td>
<td>17.35</td>
<td>10.9 +/- 0.05</td>
</tr>
<tr>
<td>Pelambres</td>
<td>Chile</td>
<td>819</td>
<td>19.78</td>
<td>10.9 +/- 0.05</td>
</tr>
<tr>
<td>Chuquicamata</td>
<td>Chile</td>
<td>193</td>
<td>5.21</td>
<td>32.3 +/- 0.2</td>
</tr>
<tr>
<td>Chuquicamata</td>
<td>Chile</td>
<td>245</td>
<td>7.82</td>
<td>31.8 +/- 0.2</td>
</tr>
<tr>
<td>Cerro Verde</td>
<td>Peru</td>
<td>3497</td>
<td>272.5</td>
<td>58.6 +/- 0.3</td>
</tr>
<tr>
<td>Cerro Verde</td>
<td>Peru</td>
<td>3060</td>
<td>168.3</td>
<td>58.9 +/- 0.3</td>
</tr>
<tr>
<td>Toquepala vein</td>
<td>Peru</td>
<td>387</td>
<td>12.43</td>
<td>57.1 +/- 0.3</td>
</tr>
<tr>
<td>Toquepala flower</td>
<td>Peru</td>
<td>1495</td>
<td>56.56</td>
<td>57.1 +/- 0.3</td>
</tr>
<tr>
<td>Tintaya</td>
<td>Peru</td>
<td>547</td>
<td>4.18</td>
<td>41.9 +/- 0.2</td>
</tr>
<tr>
<td>Sar Cheshah #3 Mo</td>
<td>Iran</td>
<td>888</td>
<td>10.23</td>
<td>13.3 +/- 0.06</td>
</tr>
<tr>
<td>Grasberg moly</td>
<td>Irian Jaya</td>
<td>2235</td>
<td>4.12</td>
<td>2.88 +/- 0.01</td>
</tr>
</tbody>
</table>
Appendix C

Analytical procedures:

Concentrations of Re and Os in all of the minerals analyzed were obtained through isotope dilution. Detailed explanation of isotope dilution can be found in Faure (1986) and Dickin (1993). Samples were loaded by the carius tube method (Shirey and Walker, 1995). Os was extracted from the solutions by a two-stage distillation process similar to Frei et al. 1998, and Roy-Barman et al. 1997. Re was purified from the distilled solutions by column chemistry. Samples were analyzed on a negative thermal ionization mass spectrometer in the Keck lab at the University of Arizona. Loading procedures are described in Chesley and Ruiz (1998).

The most difficult part in this procedure is extraction of very low concentrations of Os from the solutions in the carius tube. Problems arise because the samples are sulfides, thus dissolved sample solutions are very reduced due to large quantities of sulfur in solution. Theoretically, this can inhibit spike and sample equilibration. Therefore, we use a reverse aqua-regia (one that has more parts nitric then hydrochloric) and peroxide solutions in the carius tube to increase the amount of O in the solution. Our experiments show that use of these extra oxidizing agents enhances spike/ sample equilibration. We have also found that addition of peroxide during distillation improves the quality of the beams during analysis.

Due to the low concentration of Os in the samples analyzed, the concentration of the Os blank has a profound effect on the data. For instance, if a sample has 10ppt, and we dissolved 1 gram of sample with the blank varying from 1 to 1.5 picograms, the
measured ratios will have at least a 10% correction. This error is an order of magnitude or more than the counting statistics of the machine. Therefore, all reported values take account for this error by reporting the deviation of the isotopic ratios when the change of the blank is considered. The Re blank is not significant since the concentration of the blank has remained relatively constant at 20-35 picograms, and the samples analyzed normally contain > 400 picograms Re.

Over the three years of analyzing Os, the blanks have dropped considerably because improved cleaning procedures and overall chemistry. Table C.1 illustrates the total procedural blanks (addition of spike in the carious tube) for the three years. Regardless of the concentration of Os, the measured $^{187}$Os/$^{188}$Os remained constant through time between 0.175-0.18. In order to isolate where the blank resides, Os was measured in various amounts of acid, different parts of the distillation process, and the platinum filaments used. None of the individual tests provided a clear-cut source for the blank. Thus, the blank could reside in the carious tube, or could represent the cumulative effect of the whole process.
Table C.1- Total procedural blanks for all of the Re-Os studies

<table>
<thead>
<tr>
<th>Date</th>
<th>Os (pg)</th>
<th>Re (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec. 1997</td>
<td>6</td>
<td>31</td>
</tr>
<tr>
<td>Apr. 1998</td>
<td>4</td>
<td>38</td>
</tr>
<tr>
<td>Aug. 1998</td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>Oct. 1998</td>
<td>2</td>
<td>29</td>
</tr>
<tr>
<td>Apr. 1999</td>
<td>2</td>
<td>38</td>
</tr>
<tr>
<td>Jun. 1999</td>
<td>2</td>
<td>39</td>
</tr>
<tr>
<td>Oct. 1999</td>
<td>2</td>
<td>36</td>
</tr>
<tr>
<td>Feb. 2000</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Feb. 2000</td>
<td>1.3</td>
<td>25</td>
</tr>
<tr>
<td>Jun. 2000</td>
<td>2.2</td>
<td>12</td>
</tr>
</tbody>
</table>

Since we modified the procedure slightly for analyzing sulfides for Re-Os the following is a protocol for loading the carius tubes, running the distillations, and cleaning the savellix. The materials needed are listed and the processes are described in detail below.

**Loading Carius Tubes:**

Materials and procedure for loading carius tubes:

Carius tube
The first step in loading carius tubes is labeling each tube. Normally six tubes are used, and glass funnels are placed in the nose of the tube to facilitate addition of acids and samples. Weigh out the sample by placing it on the weighing paper. Gently pour the sample in the glass funnel by slowly tapping the sides of the weighing paper. Prepare the nitric, hydrochloric, and peroxide in 12 ml falcon tubes. The amounts of acid used depends on the sample size (table C. 2). The maximum amount of acids used without exploding the carius tubes is about 30ml of total fluid (or about half of the carius tube is full), which limits the amount of sulfide sample to a maximum of two grams. Some attempts of greater then two grams of sample did not yield the amount of predicted Os, thus indicating that sample and spike did not equilibrate at any point during the procedures. When attempting samples of greater then 0.5 grams, use larger carius tubes. The amount of pressure in tube increases drastically when dissolving more sample, since additional sulfur gas is produced in the tube.
Table C.2- Estimated amount of sample and acid needed

<table>
<thead>
<tr>
<th>Amount of Sample (g)</th>
<th>HCl (ml)</th>
<th>HNO₃ (ml)</th>
<th>H₂O₂ (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 - 0.5</td>
<td>6</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>0.5 - 1.5</td>
<td>12</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>1.5 - 2.0</td>
<td>18</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

After samples are in the carius tube freeze the alcohol bath by adding liquid nitrogen into the flask for freezing carius tubes. Add enough liquid nitrogen until the alcohol comes to a slurried state, then put the carius tube in the bath. Weigh the Os spike in the snap lid 5 ml vial, then the Re spike in the same vial. For spiking amounts refer to (Table C. 3). In order to reduce contamination, the spikes used for loading are kept in 7ml threaded vials, rather then taking the spike from the 1 liter bottle.
Table C.3- Estimated amount for spikes for various types of ore deposits

<table>
<thead>
<tr>
<th>Deposit type</th>
<th>sample (g)</th>
<th>Approx. Os</th>
<th>Os spike (g)</th>
<th>Approx. Re</th>
<th>Re spike (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low concentration</td>
<td>1 to 2</td>
<td>6-50 ppt</td>
<td>0.007 to 0.009</td>
<td>200-10000 ppt</td>
<td>0.2 to 1</td>
</tr>
<tr>
<td>Porphyry Copper</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Massive sulfides</td>
<td>0.5 to 1</td>
<td>20-900 ppt</td>
<td>0.01 to 0.04</td>
<td>100-1000 ppt</td>
<td>0.2 to 0.6</td>
</tr>
<tr>
<td>Au rich systems</td>
<td>0.1 to 0.5</td>
<td>70-1000 ppt</td>
<td>0.02 to 0.1</td>
<td>200-20000 ppt</td>
<td>0.2 to 2</td>
</tr>
<tr>
<td>Arizona wulfenites</td>
<td>0.5 to 1</td>
<td>20-150 ppt</td>
<td>0.01 to 0.04</td>
<td>200-900 ppt</td>
<td>0.2 to 0.5</td>
</tr>
<tr>
<td>Magmatic magnetite</td>
<td>0.5 to 1.5</td>
<td>15-400 ppt</td>
<td>0.007 to 0.02</td>
<td>100-2000 ppt</td>
<td>0.1 to 0.3</td>
</tr>
<tr>
<td>Chilean Mantos</td>
<td>0.5 to 2</td>
<td>6-50 ppt</td>
<td>0.006 to 0.01</td>
<td>100-10000 ppt</td>
<td>0.2 to 1.2</td>
</tr>
<tr>
<td>Porphyry Molybdenite*</td>
<td>0.04 to 0.1</td>
<td></td>
<td>0.1 to 0.4</td>
<td></td>
<td>0.3 to 0.7</td>
</tr>
</tbody>
</table>

* Concentration of Os spike is 1.11 nanograms per gram, the spike is enriched in $^{185}$Os

* Concentration of Re spike is 6.72 nanograms per gram, the spike is enriched in $^{185}$Re

* Molybdenite spikes are higher concentrations of similar spikes of Os milligrams per gram and Re milligrams per gram

Pipette the spikes into the carius tube via the funnels, then pour the hydrochloric acid in the 5 ml snap lid to rinse the savillex. Pipette at least 2ml of hydrochloric acid (using the same pipette tip) into the carius tube to ensure that the spike is in the carius tube.
Completely freeze spikes, and hydrochloric acid, you can add more liquid nitrogen if the mixture is not cold enough. After frozen add the nitric and peroxide and freeze these.

Once the acids are frozen, seal the nose of the carius tube with the torch by warming the nose of the tube with a blue flame and then seal by increasing the temperature of the flame and focusing on the opening of the carius tube. Rotate the tube at a constant pace throughout the sealing procedure. Immediately place the carius tube in the hood after sealing. If the seal was not good enough or the sample becomes very reactive the seal can break and acid will flow out of the tube.

After the samples have warmed to room temperature (which is about 2 hours after sealing), put the samples in a metallic pipe bomb (size of the pipe bomb depends on the size of the carius tube). Place pipe bombs in the oven overnight at 200°C.

Distillation

Materials and procedure for distillation

6- 64ml threaded teflon vials with distillation caps 6 medium, threaded 120ml teflon jars
6- threaded 17ml teflon flat bottomed vials 10 feet FEP heavy walled tubing 1/8

teflon boiling chips aluminum foil
6 Falcon tubes with 5 ml 3 times 8N nitric acid hydrogen peroxide
Nalgene tubing 1/4 ID, 3/8 OD, 1/16 W 6 10cc poppropylene glass
syringe HBr Stand-two types (Picture 2)
Tupperware rectangular box at least 5 inches deep 6 Falcon tubes (with punctured lids) 12 Twisty ties
metal rod to score carius tubes
liquid nitrogen and flask with alcohol ice
6 1-22ul pipette tips Exacto knife and scissors
Nitrogen tank and regulators Flat thermomenter
Aluminum block (machined to fit distillation sav.) Chem. Wipes
Y connectors Hot plate
1000ml Beaker for carius tubes to warm

The key to a successful distillation is to have all of the material prepared and assemble them slowly. This protocol will highlight each step thoroughly. First, prepare the 6-64 ml distillation savillex by threading the tubes with enough tubing (FEP heavy walled), so that when closed the tubing nearly touches bottom of savillex tube. Since the fit of the tubing can be very tight, cut the tubing on an angle and slightly wet it (with MQ) so as to ease the process of threading the tubes. Set the distillation savellix in the aluminum block and put it on the hot plate.

Next prepare the 6 glass syringes with peroxide that will be added to the distillation. Put about 12ml of peroxide into a falcon tube. Grab the syringe (plunger completely compressed), and tilt the falcon tube to nearly horizontal to the lab counter. Slowly draw 3-5 ml of peroxide from the falcon tube to the syringe. After all six syringes are filled, cut 6 one-inch pieces of Nalgene tubing. Connect the syringe to a branch on the Y connection. Next, connect the one-inch tubing to the stem of the connection put a
1-200µl pipette tip in the end of the Nalgene tubing. Connect the last branch of the Y connection to the nitrogen flow. Use the twisty ties to attach the syringes to the post in an upright position. Put the nose of the pipette tip in the tubing of the distillation savellix.

Now finish making the connections for the distillation by preparing the HBr. Puncture the lids of 6 falcon tubes with scissors. Place these flacon tubes in the custom made tupperware bin, and set this on a stand. Cut 6 1-foot long pieces of FEP heavy walled tubing with the exacto knife. Connect tubing with the other end of the distillation savellix and the punctured lid of the falcon tubes that are in the custom made tupperware. Take the lid off of the tupperware and fill the bin half full with ice and water mixture (add enough ice to keep water cold for at least three hours). Carefully add 8-9 ml of HBr to the Falcon tubes that are sitting in the ice bath. After all six are filled, turn the nitrogen and slowly bleed the nitrogen gas until the HBr in the Flacon tubes is bubbling.

Next, open the carius tubes. Prepare a bath in 1000 ml beaker for the carius tubes to warm in, get the beaker and fill with ice and water mixture about 2/3 full. Freeze the carius tubes, this can be done two ways, either directly emerging the tubes in liquid nitrogen, or freezing the alcohol bath. After the tube is completely frozen, score the nose around the perimeter of the carius tube. Place carius tubes in the hood and break the nose of the tube along the place where it is scored. Place the cracked tubes in the water bath in order to warm them. Some samples tend to be reactive when opening, so watch the tubes warm. While the carius tubes warm to room temperature (usually 10 minutes or so) place 10-20 small teflon boiling chips in the bottom of the distillation beaker.
Once the tubes have warmed take carius tube out of the bath with a chem. wipe and carefully pour contents in the distillation savillex. In order to reduce contamination, place a chem. wipe on the tops of the other distillation savillex. Then, place the lid of the savillex which you are adding the sample on the chem wipe. Proceed with this process quickly as to ensure that no Os has become a volatile and lost. Rinse the carius tube with 5 ml 8N nitric in the falcon tube, and swirl acid in the tube and pour the contents into the distillation beaker. In order to add the nitric without spilling acid, pour slowly. After loading six tubes, check each HBr falcon tube to assure that they are receiving nitrogen and bubbling, and then wait for at least 10-15 minutes. During this time the HBr might become slightly discolored to an almost chocolate brown. After 15 minutes slowly add the peroxide. Some solutions become very reactive during this step, so proceed with care and be prepared to change the nitrogen flow with each one of the regulators. Wait another 10-15 minutes after adding peroxide before raising temperature. Raise temperature of the aluminum block to about 110°C. At about 30-40°C the solutions become reactive again because of O release so be careful when regulating the nitrogen flow. Let the experiment distill for at least 1 hour at 110°C. Watch the experiment to make certain that nitrogen flow is constant throughout the experiment, condensation commonly occurs on the lids of distillation beakers and inhibits proper flow of nitrogen and potentially OsO species.

Prepare the savellix for the Re and Os solutions. Record and label the Os (17ml threaded teflon vial) and Re (medium 120ml jar) savillex. Wrap teflon tape around the lids of the Os savillex. After 1 hour at 110°C turn the temperature off and take the HBr
solutions out of the Falcon tube and place in Os savillex and wait until block cools completely before placing Re solution in Re beaker. Place the Os savillex under heat lamp at 80°C for at least 3 hours, then remove lid and dry down overnight. Uncap the cooled Re solutions and dry down overnight.

Microdistillation

Materials and procedures for microdistillation

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity</th>
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</thead>
<tbody>
<tr>
<td>Conical sav.</td>
<td></td>
</tr>
<tr>
<td>1 time distilled HBr</td>
<td></td>
</tr>
<tr>
<td>Pipettes and tips</td>
<td></td>
</tr>
<tr>
<td>Chromerge(CrO₃)</td>
<td></td>
</tr>
<tr>
<td>Aluminum foil</td>
<td></td>
</tr>
<tr>
<td>Thermometer</td>
<td></td>
</tr>
</tbody>
</table>

We follow the method in Roy-Barman et al. (1998). Open the conical savillex and pipette about 0.015 to 0.016ml of Hbr into the tip of the conical. Open the Os (17ml) savillex and pipette in about 0.025-0.028ml of chromerge in the base of the savillex. Pipette the chromerge out of the 17ml Os beaker and place on the lid of the conical savillex. Carefully screw the conical part to the lid (have the lid facing up so as not to move the chromerge). Wrap aluminum foil around the conical, and place conical savillex on hot plate and turn heat to 80°C. Let the experiment sit at temperature for at least 2 hours. After two hours take foil off and carefully unscrew lid. Place the conical part of the savillex in the dry box and wash the chromerge on the lid with MQ.

Cleaning Procedures:

All savillex experience a four stage cleaning procedure. After use all savillex are rinsed with MQ water, and then nitric acid is added in the containers. They are placed on a hot plate and heated for at least two days. The exception to this part of the cleaning is the Os conicals, HBr is used in this step rather then nitric. After two days or more, the
acid is discarded and the savillex is placed in a sulfuric bath (this bath also has a one package of NoChromix added). Savillex are kept in the sulfuric bath for 2 days or more.

Next the savillex are taken out of the sulfuric acid and thoroughly rinsed with MQ water and placed in a bath of nitric acid. This bath is heated and they are kept in the bath for a few days. Finally, the savillex are taken out of the nitric and rinsed with MQ water and placed in a MQ bath. Once out of the MQ water the savillex are wrapped in Saran Wrap for storage.

References:


Appendix D: Location Maps

This section contains generalized location maps for the deposits studied.
Figure D.1 - Location Map of Chilean Ore Deposits
* Approximate position of basement marked by dashed line
Figure D.2- Location map for Peruvian Porphyries

Figure D.3- Location Map for Panguna
Figure D.4 - Location Map for Nickel Plate
Appendix E: Supplementary Data

This section of the thesis contains information that describes the results for supplementary analyses from the deposits studied in chapters 2-5, and provides descriptions of related deposits.

South Pacific Deposits:

Grasberg:

In order to further establish crustal links with gold rich ores present in the Grasberg, samples of mechanically separated pure gold (G-1); sedimentary rocks bordering the intrusions and chalcopyrite from the Main Grasberg Intrusive unit (cpy-MGI) were analyzed. The sample of pure gold was machine separated by Freeport MacMoRan. The sedimentary rocks were crushed to a fine grain size for analyses, and the chalcopyrite was prepared as discussed in chapters 2-5.

The pure gold sample contains 873 ppt Os and 600 ppt Re, the sediments range from 10-400 ppt Os, and the chalcopyrite has 60 ppt Os and 80 ppt Re. The initial $^{187}\text{Os} / ^{188}\text{Os}$ values for the gold and chalcopyrite are 1.23 and 0.87 respectively, and both fit on the mixing trend developed in chapter 4. The measured $^{187}\text{Os} / ^{188}\text{Os}$ ratios for the sedimentary rocks vary from 0.5-1.6.

The elevated $^{187}\text{Os} / ^{188}\text{Os}$ value of the gold and high concentration of Os indicates a crustal source (most likely sedimentary shale) for free bound gold in the deposit. On the mixing curve (Fig. E.1), the pure gold sample (G-1) occurs near the heavy sulfide sample with the greatest gold content. The pure gold result indicates that gold from the Grasberg has a large component of the gold rich ores found in the massive sulfide. Exact
proportions of the bulk contributor of the gold are complex, however the gold rich ore with the sedimentary signature appears to dominate the gold metal budget. This result strengthens the evidence for shales as a probable contributor for gold in the deposit. The chalcopyrite sample from the MGI also lies on the mixing trend and indicates that its origin is similar to the massive sulfide.

Verification of the sedimentary source for the ores is further solidified by the Os analyses of sedimentary rocks. Spencer Titley, Stacie Gibbins, and Kurt Friehauf collected a suite of unaltered sedimentary rocks along the road leading to the mine. The samples selected could have affected the magmas during their ascent, or while they cooled and the hydrothermal system was active. The stratigraphic relationships along with the Os data are in figure E.2. All measured ratios are identical or greater than the initial value calculated for the stockwork intrusions. This indicates that these sedimentary strata could be viable candidates for the enriched signature evident in the ores. Exact proportions for which source most likely contributed is difficult to estimate because rock/fluid partition coefficients for Re and Os have not been calculated.

The $^{187}$Os/$^{188}$Os value measured for the Kopai formation shale is identical to the initial $^{187}$Os/$^{188}$Os values for the stockwork. This relationship may indicate that this shale is responsible for the Os signature throughout the deposit. Thus, the data could reflect an instance in which a porphyry served as a heat engine that leached metals from various crustal rock reservoirs and redeposits them in economic concentrations.
Panguna:

The samples from Panguna were taken from Chris Eastoe's thesis collection (Eastoe, 1979). We sampled various alteration sequences in the deposit, and the exact relationships are in appendix B. Panguna is located on Bougainville, an island east of Irian Jaya, Indonesia, the northernmost of the Solomon Islands, and part of Papua New Guinea (location map in appendix D). The deposit is classified as a Cu-Au porphyry deposit that formed in an island arc setting due to recent tectonic activity in the South Pacific. The ore body is associated with Pliocene quartz diorite-granodiorite intrusions that crosscut previously formed basaltic-andesite volcanism. Detailed descriptions of the geology and evolution of the deposit are in Eastoe (1982, 1978), Ford (1978), and Fountain (1972).

For the purpose of this study, the island arc environment in which Panguna formed is different than the continental arc settings of the other deposits studied. The deposit’s geology is similar to that of other island arc porphyries of the area and is most likely representative of porphyries that formed in this island arc environment. The concentrations of Re and Os in the deposits are similar to those seen in the Chilean arc, with Re ranging from 0.2-15 ppb and Os from 5-7ppt.

The data form an errorchron with an age of 2.2Ma ± 2 Ma, and an initial $^{187}\text{Os}/^{188}\text{Os}$ of 0.14 ± 0.12. Thus, the data does not constrain reliable age or source information. There has been extensive Ar chronology for the deposit and it suggests that mineralization occurred between 2-3Ma, and perhaps slightly older (Fountain, 1972). If
the age information from Ar chronologies is used for determining specific initial ratios for each sulfide analysis, then the range of initial $^{187}\text{Os}/^{188}\text{Os}$ is 0.12-0.2.

The source of Os according to this plot is predominantly mantle, since the arc mantle measured by McInnes et al. 1999 has Os isotopic compositions that vary from 0.12 to 0.17. McInnes et al. (1999) measured $^{187}\text{Os}/^{188}\text{Os}$ values for the mantle is much greater than the expected 0.13 (Meisel et al. 1996). They interpreted that some portions of the arc mantle in this portion of the South Pacific had been metasomatized by fluids that leached radiogenic Os from subducted sediments, and that this mantle can have elevated $^{187}\text{Os}/^{188}\text{Os}$ ratios. They found this type of mantle signature in the gold ores from Lihir (related gold deposit near Panguna, near New Ireland, north-west of Bougainville), and concluded that the metasomatized mantle predominates the source for Os and other metals in the deposit. The $^{187}\text{Os}/^{188}\text{Os}$ initial ratios from Panguna provide further evidence for a similar type mantle source for the ores at Panguna. Figure E.3 graphically illustrates the mantle signature reflected in these ores.

**Andean Ore deposits**

**Escondida:**

The geology of the deposit is described by Padilla et al. (in press), and is similar to the porphyries of Oligocene age in the Chilean belt. Ruiz and Mathur (1999) reported that sulfides from the various alteration events in Escondida could not provide reliable source information because of the high concentrations of Re present in all samples. These results could reflect the affects of supergene alteration that opened the Re-Os system or the presence of trace quantities of molybdenite in the sample. There is
evidence for the latter possibility because ICP-MS analysis of the ores indicates elevated concentrations of Mo in the sulfides. However, molybdenite was not detectable in microscope or microprobe level, thus the quantities of the molybdenite present in the sample must be extremely small.

In order to overcome the difficulties encountered with sulfides, magnetite from the two mineralizing plutons and hydrothermal magnetite were analyzed for source information. The objective for analyzing these samples is to reveal what magma source was responsible for mineralization, and to compare the source of metals of Escondida with other Oligocene porphyries. Caution must be used in interpreting the data because the calculated concentrations of Re and Os for the magnetites are an overestimation for the whole rock, but the genetic information obtained remains relatively constant. In order to constrain accurate source information for these samples; concordant U/Pb ages (37.5 Ma) from zircons in rock samples were used to resolve initial $^{187}$Os/$^{188}$Os values.

The concentrations of Re vary from 2 to 40 ppb and Os vary from 12-60ppt. Esc-1 is the first intrusive (i.e. the older) event in the system, and it has the highest concentration of Os and Re and the highest initial $^{187}$Os/$^{188}$Os of 1.5. The second event Esc-2, has lower concentrations of Re and Os than the first event and a significantly lower initial $^{187}$Os/$^{188}$Os of 0.30. The hydrothermal magnetite has the lowest concentrations of Re and Os and an initial value that lies between the Esc-1 and Esc-2 of 0.68.

The results are plotted in figure E.4, and illustrate that the hydrothermal event lies between both intrusive events. There are two possible explanations for the data. First,
the hydrothermal magnetite (i.e. mineralization) is a unique event unrelated to Esc-1 and Esc-2. However, field evidence would not support this conclusion.

The second explanation is that the hydrothermal magnetite is a mixture of the granodioritic magmatic events of Esc-1 and Esc-2. Geologic evidence from the deposit favors this interpretation. Determination of which system (Esc-1 or Esc-2) provided the bulk of the metals is complex. The difficulty resides in postulating end member concentrations of Os in each of the fluids responsible for mineralization. In general, the concentration of the elements and radiogenic signature in Esc-1 was much greater than seen in Esc-2. Therefore, in order for the second event, Esc-2 (less radiogenic, and lower concentration), to have a significant input to the Re-Os budget it must have contributed a larger portion of metals in order to produce a value of 0.7 as seen in the hydrothermal magnetite. This conclusion is speculative, however the evidence may indicate that the less radiogenic event (Esc-2) supplied a majority of the metals present in the deposit.

Chuquicamata and Spence:

The geology and previous Re-Os analyses from Chuquicamata is reviewed in chapter 5. The new data further illustrate the two sources seen in the deposit because they lie on the isochrons previously developed. Two results from chalcopyrite (Chuquihypo) further solidify the lower initial $^{187}\text{Os}/^{188}\text{Os}$ of 0.15. Also, two sphalerite (Chuquispahal) analyses fall on the isochron with the higher $^{187}\text{Os}/^{188}\text{Os}$ initial value of 1.01. The statistics of the isochron and the age change slightly with the addition of the sphalerite samples, however the initial value remains constant. Therefore, the sphalerite has a
similar source as seen for the other minerals associated with this younger, more radiogenic event.

Spence was discovered relatively recently (in the 1990's) by Rio Algom Mining Company and the information about the basic geology is forthcoming. The deposit is located 40-50 Km directly west of Chuquicamata, and preliminary Ar dates from the mining company suggest that it formed during the Paleocene. The one Re-Os result indicates that the source for metals is crustal (initial $^{187}\text{Os}/^{188}\text{Os}$ of 5), and very similar to that seen in the Paleocene porphyries of northern Chile and southern Peru.

Toquepala and Cuajone:

These two deposits lie to the north of all the Chilean deposits analyzed (map in appendix D). The basic genesis of the deposits is similar to that of the Chilean examples, and discussion of the geology and evolution of the deposits can be found in (Sillitoe, 1989, 1990; Zweng and Clark, 1995, Clark et al. 1990 a, b).

Only two low concentration samples were analyzed and the concentrations of Re and Os are 6-93 ppb and 8-36ppt respectively. The measured ratios are highly radiogenic (50-100), and the Re/Os ratios are large. Calculated initial $^{187}\text{Os}/^{188}\text{Os}$ values for the deposits were solved by using the molybdenite ages in appendix B. The initial $^{187}\text{Os}/^{188}\text{Os}$ values for both deposits are similar, and near 50.

None of the other porphyries analyzed have measured or initial values this high. These deposits occur in the Arequipa terrain (Richards, 1995). This block of crust is much older and thicker than the basements seen in the Chilean deposits. Perhaps these
radiogenic signatures are reflecting extensive interaction with the volcanic and sedimentary rocks of the Arequipa terrane.

**Canada:**

**Hedley district Cu-Au skarns, British Columbia**

The Hedley district skarns lie about 200 Km east of Vancouver (map in appendix D), and reside in the Quesnel terrane (Wheeler et al. 1991) of the Intermontane belt in southern British Columbia, Canada. Conventional thought has mineralization tied to the gabbroic-dioritic intrusions that invaded thick sedimentary strata of Triassic to Jurassic age. These intrusions formed either on the rifted eastern margin in a marine back-arc basin, or on the edge of an intrabasinal platform (Ray et al 1996). The geology and hydrothermal evolution of the deposit is described in (Ettinger et al, 1992, Ray et al, 1996).

Gold rich (70-100ppm Au) and gold poor (10-20 ppm Au) arsenopyrite and pyrrhotite from the productive mines have concentration of Re that range from 4-93ppb, and Os that range from 150-670 ppt. Arsenopyrite from the Canty and Nickel plate mine form an isochron with an age of $217 \pm 17$Ma and an initial $^{187}$Os/$^{188}$Os of $1.7 \pm 0.34$ (Fig. 6.5). This age correlates within error of the ages of 217Ma (Ray et al. 1995) and 198 Ma (Parrish and Monger, 1991) determined on zircons from the related diorites. The pyrrhotite sample does lie on the isochron, and calculated initial $^{187}$Os/$^{188}$Os is slightly higher at 2.4.
The geological significance of the age determination is that mineralization is linked with the older intrusive events of the Hedley stocks (~217 Ma) rather than the younger volcanic events of the Bromley Batholith and Mount Riordan stock (~180-198 Ma). This distinctly places mineralization in association with the island arc volcanism before the terrane boarded around 170 Ma (Harris et al. 1998).

Major and trace element data from the volcanic rocks associated with mineralization illustrate primitive signatures for the magmas (Ray et al. 1996). Previous studies link the source of metals directly to the primitive magma (Ettlinger et al., 1992). The Re-Os data provide a different perspective than this magmatic association. The initial $^{187}\text{Os}/^{188}\text{Os}$ of the isochron is around 1.7 and much greater than the present chondritic mantle of 0.13.

These data indicate a crustal source for the metals in the deposit. Small amounts of crustal contamination during the magma’s ascent could explain this radiogenic signature, however appropriate crustal sources probably did not exist in this environment. In the hypothesized island arc environment, the only radiogenic sources for Os could be the slab and a metasomatized mantle. These end members do not contain enough Os and an elevated radiogenic signature to explain the concentrations and radiogenic component present in the ores (Fig.E.6).

As highlighted in chapter 3, black shales can easily resolve high concentration, radiogenic data. The Hedley volcanics intruded into a basin that contains argillaceous shales and other sediments of upper Paleozoic and Lower Mesozoic age (Ray et al. 1996, Ettlinger, 1992). The sedimentary rocks provenance resides to the east, and they contain
eroded remnants of greenstone belts and other younger arc materials. It has been suggested by Titley (1991) that sedimentary strata can be enriched in gold, and that these pre-enriched sedimentary rocks serve as a metallic reservoir for ore bearing fluids. The elevated concentrations Re and Os and the evolved $^{187}\text{Os}/^{188}\text{Os}$ signature of the both gold rich and gold poor ores of Nickel Plate indicate that sedimentary rocks could be the source for the economic elements of interest.

In comparison to the massive sulfide ores at Grasberg, the Nickel Plate results indicate that the mineralizing fluid was isotopically homogenized throughout the hydrothermal system because samples taken from various parts of the ore deposit form an isochron. The only indication of mixtures or disequilibrium is seen in the pyrrhotite that has a slightly higher initial $^{187}\text{Os}/^{188}\text{Os}$. The relevance of this observation is that the fluids that leached the surrounding sediments achieved equilibrium, similar to porphyry copper fluids. Fluid inclusion evidence from (Ettlinger et al. 1992) found that the fluids were in the range of typical porphyry copper fluids of 460°C-480°C, and certain inclusions revealed temperatures as high as 800°C. The Re-Os data support the notion that the intrusion served as a heat source and promoted the evolution of an isotopically homogenized fluid that leached and concentrated metals from the surrounding sedimentary column.

References:


Table E.1 - Re-Os supplementary data for the deposits studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Re (ppb)</th>
<th>Os (ppt)</th>
<th>$^{187}Re/^{188}Os$</th>
<th>$^{187}Os/^{188}Os$</th>
<th>$^{187}Os/^{188}Os$</th>
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</thead>
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<td>Ni Plate-1</td>
<td>B.C.</td>
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<td>5086 +/- 450</td>
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<td>1.65 +/- 0.2</td>
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<td>B.C.</td>
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<td>223</td>
<td>14109 +/- 1250</td>
<td>54.5 +/- 2.1</td>
<td>1.65 +/- 0.2</td>
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<td>Canty-2</td>
<td>B.C.</td>
<td>69.733</td>
<td>673</td>
<td>791 +/- 55</td>
<td>4.61 +/- 0.81</td>
<td>1.65 +/- 0.2</td>
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<tr>
<td>Canty-3</td>
<td>B.C.</td>
<td>93.727</td>
<td>630</td>
<td>1259 +/- 100</td>
<td>5.93 +/- 0.17</td>
<td>1.65 +/- 0.2</td>
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<tr>
<td>Canty-1</td>
<td>B.C.</td>
<td>4.862</td>
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<td>50.2</td>
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<td>MGI Gras</td>
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<td>60</td>
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<td>pan-cpy</td>
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<td>2956</td>
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<td>143.09</td>
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<td>Escal- ELN-1</td>
<td>Chile</td>
<td>45.848</td>
<td>74</td>
<td>3502.6 +/- 120</td>
<td>1.474 +/- 0.07</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Table 1- Complimentary data for the deposits studied. PCO= porphyry copper deposit, 1= initial ratio, mag= magnetite, Sphal= sphalerite, cpy= chalcopyrite, Esc.= Escondida, B.C.= British Columbia, Canada, Escal= Escalones, Gras= Grasberg, Pan= Panguna
Figure E.1 - Mixing relationships at the Grasberg with the gold and chalcopyrite samples from the MGI


<table>
<thead>
<tr>
<th>Lithology</th>
<th>Formation</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alduna Fm.</td>
<td>1750±200 m</td>
<td></td>
</tr>
<tr>
<td>Modio Fm.</td>
<td>1000±200 m</td>
<td>2000±400 m</td>
</tr>
<tr>
<td>Tuaba Fm.</td>
<td>950±100 m</td>
<td>3500±1000 m</td>
</tr>
<tr>
<td>Kariem Fm.</td>
<td>500±200 m</td>
<td>6500±1000 m</td>
</tr>
<tr>
<td>Awinagin Fm.</td>
<td>&gt;2000 m</td>
<td>&gt;6000 m</td>
</tr>
</tbody>
</table>

- Alduna Fm. | 1750±200 m |
- Modio Fm. | 1000±200 m | 2000±400 m |
- Tuaba Fm. | 950±100 m | 3500±1000 m |
- Kariem Fm. | 500±200 m | 6500±1000 m |
- Awinagin Fm. | >2000 m | >6000 m | ? |

187\text{Os}/188\text{Os}_m Os ppt

\[\begin{array}{lll}
0.80 & 400 \\
0.54 & 263 \\
0.52 & 201 \\
2.2 & 10 \\
1.44 & 7 \\
1.56 & 18
\end{array}\]

E.2- Stratigraphic section of sedimentary rocks that Grasberg intersected and their Os concentrations and ratios
Figure E.3- Panguna Data with reference to the mantle
Figure E.4-Plot of calculated initial $^{187}$Os/$^{188}$Os values from Escondida Magnetites
Figure 6.5- Isochron plot of the Ni Plate data

Age - 217Ma +/- 16
MSWD 1.52

$^{187}\text{Os} / ^{188}\text{Os}$ initial = 1.65 +/- 0.3
Figure E.6 - Os concentration versus Re/Os ratio comparison of sulfides in ore deposits and geologic reservoirs, note black shales only source with high concentration of Os and a radiogenic signature, data taken from literature.