Re-Os isotope systematics of sulfides from felsic igneous rocks: Application to base metal porphyry mineralization in Chile

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ABSTRACT

Dating sulfides and determining the source of ore-forming metals have been limiting factors in our understanding of processes that produce hydrothermal ore deposits. Here we analyze sulfides from base metal porphyry deposits from Chile to demonstrate the potential of the Re-Os system to determine both the age and the source of metals for hydrothermal mineralization. Cogenetic chalcopyrite, bornite, pyrite, and sphalerite from El Teniente (ca. 5 Ma) have $^{187}Re/^{188}Os$ ratios from 0.3 to 21.8 and initial $^{187}Os/^{188}Os$ ratios from 0.17 to 0.22. A paragenetically late pyrite that has an initial $^{187}Os/^{188}Os$ of 0.88 indicates that the ore deposit is not isotopically homogeneous in Os throughout the formation of the deposit. Pyrite samples from Andacollo (ca. 100 Ma) have $^{187}Re/^{188}Os$ ratios from 15 to 3600, and different isochrons yield ages between 87 and 103 Ma, consistent with different sericite K-Ar ages. Initial $^{187}Os/^{188}Os$ ratios of 0.2 to 1.1 are similar to those of El Teniente. The relatively homogeneous $^{187}Os/^{188}Os$ ratios (~0.19) for cogenetic sulfides from El Teniente suggest that most of the Os in the ore was from the causal intrusive. The late-stage pyrite probably incorporated Os leached from the country rock by meteoric fluids, which mixed with magmatic fluids at the periphery of the hydrothermal system. We demonstrate that the Re-Os isotope system can be a powerful geochronological tool in hydrothermal ore deposits. The large range in Re/Os ratios of sulfides permits the age of mineralization to be well constrained, despite isotopic heterogeneities of the hydrothermal fluids.

INTRODUCTION

Among the central questions in metallogenetic studies are the age of mineralization and the source of the ore-forming elements. Answering either of these questions is notoriously difficult. Past attempts to date ore deposits have relied on isotopic studies (Rb-Sr, Sm-Nd, U-Th-Pb) of spatially associated gangue minerals or wall-rock alteration, but it is not always obvious how these minerals relate to ore formation. An exception is sphalerite from Mississippi Valley–type deposits, which has been dated by the Rb-Sr isotope system (Nakai et al., 1990; Brannon et al., 1992). The potential application of Re-Os isotopes to geologic problems has been recognized for decades (Herr and Merz, 1955; Herr et al., 1967; Schindler, 1975; Allègre and Luck, 1980; Luck and Allègre, 1982), but only in the past few years has its potential begun to be realized. Re and Os are chalcophile and siderophile (Martin et al., 1993), in contrast to the lithophile affinities of Rb-Sr, Sm-Nd, and U-Th-Pb. Consequently, the Re-Os system is uniquely suitable for metallogenetic studies, because it can be applied directly to the sulfide minerals, rather than associated phases.

Re-Os isotopic dating of molybdenite has been shown to be very robust (McCandless et al., 1993; McCandless and Ruiz, 1993; Yin et al., 1993), but few studies have attempted to analyze other sulfides from felsic igneous rocks, because of their low Os and Re concentrations (Schindler, 1975; Morgan et al., 1968). New methodologies now allow precise measurement of sub–part per billion levels of Os and Re, which permits the dating of more common sulfides (Morgan and Walker, 1989; Volkening et al., 1991; Creaser et al., 1991; Shen et al., 1996; Ruiz et al., 1997).

In addition to its geochronologic potential, the Re-Os isotopic system may be an important tracer for the source of the ore-forming elements. Questions as to whether metals are derived from country rocks or magmas, and if magmatic, whether the magmas are mantle or crustally derived are fundamental questions in metallogenesis. Because Os is compatible to highly compatible relative to Re during partial melting of the mantle (Walker, 1988, 1989a, 1989b), the products of mantle melting have high Re/Os ratios. Consequently oceanic and continental crust evolve to greatly elevated $^{187}Os/^{188}Os$ ratios over time, as compared to the mantle, due to the decay of ^{187}Re to ^{187}Os. Thus, Re-Os isotopes are a potentially powerful tool for documenting interactions between the crust and mantle.

The data presented here demonstrate the power of Re-Os isotopes for geochronologic and genesis studies of common sulfides, and indicate the overall potential of the isotopic system for metallogenetic studies. Such studies may also profoundly affect our understanding of sulfide precipitation in any environment, including diagenesis and magmatic-hydrothermal systems.

ANALYTICAL TECHNIQUES

Approximately 1 g samples of bornite, chalcopyrite, pyrite, or sphalerite were digested in a Carius tube at 240 °C overnight in a 1:2 solution of $HCl:HNO_3$. The procedure is similar to that of Shirey and Walker (1995), but modified for sulfides to ensure complete oxidation of the samples in the Carius tube. The technique used here yields total Os contents from 50 pg to 1 ng and Re contents from 50 pg to 100 ng to be analyzed by negative thermal ionization mass spectrometry (NTIMS).

The Carius tube solution is treated in a two-stage distillation procedure similar to that described by Shirey and Walker (1995), but also modified for sulfides to ensure complete oxidation of Os to a tetroxide. This is critical to achieve equilibrium with the spike during the digestion process, and to mobilize the Os during the distillation stages. This was accomplished by using 30 ml of 15M HNO_3 and 11 ml of H_2O_2 rather than H_2SO_4-H_2O_2 in the first stage distillation. The second-stage distillation is the same as that of Shirey and Walker (1995); Os is trapped in the second stage either in HBr or in a 3:1

mixture of 10M HCl:ethanol. The Os trapped in the second trap is heated at 70 °C overnight in a sealed Savillex beaker to ensure that the Os is in the reduced chloride or bromide form before drying the sample. The residue is brought back in solution in 0.1M HCl and loaded on micro-anion columns for additional purification (R. A. Creaser, 1995, personal commun.).

The Re remains in solution in the first flask of the first distillation. The Re solution is dried-down, and the cake redissolved in a 0.1M HNO_3 solution, which is then loaded on a 1 ml anion column (AG-1 X8, 200–400 mesh). The procedure is similar to that described by Morgan et al. (1991) and Morgan and Walker (1989), except that the first-stage Re-column chemistry uses HNO_3 instead of H_2SO_4. This procedure is repeated using 0.1 ml anion resin.

The samples are loaded on platinum filaments and analyzed by NTIMS on a VG 54 mass spectrometer (Creaser et al., 1991). Total Re blanks range from 14 to 36 pg. Total Os blanks are 4 pg. Absolute quantities of Re and Os measured on the NTIMS are very low (Table 1) and the errors are usually between 0.5% and 1% based on replicate analyses. We believe some of the cause for the uncertainties is elemental inhomogeneity. Standards with similar concentrations reproduce to better than 0.1%.

GEOLOGIC SETTING OF THE CHILE Cu ORE DEPOSITS

The ore deposits studied here were emplaced in a collage of sedimentary, igneous, and metamorphic rocks which were accreted along the Chilean margin from the Carboniferous to Late Cretaceous (Davidson and Mpodozis, 1991; Sillitoe, 1991). A convergent setting has existed since the Precambrian, but stresses in the continental lithosphere have shifted from compressive to extensional, the latter case being attributed to a steeper angle of subduction of the oceanic plate (Mariana-type subduction; Davidson and Mpodozis, 1991). Magmatic arcs have formed since the Late Cretaceous, migrated eastward, and are the settings in which the major base metal porphyry deposits formed. With respect to country rocks, the Chilean deposits are dominantly emplaced in granitic rocks of Mesozoic and Paleozoic age, unrelated to the porphyry magmatism.

Andacollo is the oldest economic base metal porphry in Chile with an age of ca. 100 Ma. It consists of a typical base metal porphyry but has distal gold mineralization in stratabound mantos (Munizaga et al., 1985; Reyes, 1991). The copper mineralization is hosted in a tonalite porphyry stock. The main economic mineralization is chalcopyrite accompanied by potassic and sericitic alteration (Llaumett et al., 1975). Sericite K-Ar dating for pyrite-chalcopyrite-chalcocite assemblages of the base metal porphyry yields two ages: 104 ± 3 Ma and 98 ± 2 Ma. Sericite from the spatially associated gold mineralization yields a 91 ± 6 Ma age.

El Teniente is the youngest porphyry base metal deposit in Chile, ca. 5 Ma (Clark et al., 1983; Cuadra, 1986). The mineralization is hosted in a quartz diorite and dacite porphyry and contains predominantly chalcopyrite and bornite along with potassic alteration of the host (Camus, 1985) (Fig.1).

RESULTS AND DISCUSSION

Sulfides from El Teniente were selected because the young age of mineralization (ca. 5 Ma) requires minimal corrections for the growth of ^{187}Os from the radioactive decay of ^{187}Re, reducing uncertainties in the initial $^{187}Os/^{188}Os$ ratios. This characteristic allows the opportunity to evaluate the source(s) of Os in the fluids and their evolution. Furthermore, a detailed mineralogical sampling of the deposit can be used to evaluate the distribution coefficients of Re and Os between different phases and hydrothermal fluids.

Sulfides from sample TEN11-95 (chalcopyrite and sphalerite) were separated to investigate the Re and Os behavior between cogenetic minerals. Several splits of chalcopyrite from this single hand specimen have concentrations of Re that range from 0.05 to 0.12 ppb and Os concentrations that range from 0.08 to 0.9 ppb (Table 1). The large ranges in concentrations suggest that crystallographic constraints do not control the distribution of Re and Os. The sphalerite from the same sample has Re and Os contents and $^{187}Os/^{188}Os$ ratios within the ranges of the chalcopyrite.

The $^{187}Os/^{188}Os$ ratios of the chalcopyrite, sphalerite, and bornite samples from El Teniente plot between 0.17 and 0.22 on an Os isochron diagram. The flat slope of the errorchron reflects the very young age of the deposit. A pyrite sample with a more radiogenic $^{187}Os/^{188}Os$ ratio of 0.88 exhibits textural features suggesting that the mineral formed after the other sulfides. These data can be used to constrain the source of the ore-forming metals. The first question about these magmatic-hydrothermal systems is whether the metals originated from the magma or were transported by hydrothermal fluids. If the metals were derived from magmatic fluids, then one would need to investigate the evolution of the magmas and source of the magmatic components. The relatively homogeneous $^{187}Os/^{188}Os$ ratios for the sulfides of El Teniente suggest that most of the Os was provided by the causal intrusive and not from the surrounding country rocks. In addition, the $^{187}Os/^{188}Os$ ratios of the sulfides (~0.19) are not significantly more radiogenic than the mantle Os, indicating that this causal felsic magmatic system had a significant mantle Os component. It is important to note, however, that significant amounts of felsic crust would be needed to affect the mantle isotopic values because of the small concentrations of Re and Os in the crust relative to mantle melts. The more radiogenic sulfides ($^{187}Os/^{188}Os \approx 1$) are probably precipitated from meteoric fluids that

TABLE 1. RE-OS ISOTOPIC DATA FOR SULFIDES FROM CHILE

Sample name	Total Os (ppb)	Total Re (ppb)	$^{187}Os/^{188}O_m$	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os_i$
El Teniente					
TEN11-95-cpy (27)	0.082	0.116	0.194	7.8	0.193
TEN11-95-cpy (17)	0.874	0.053	0.196	0.32	0.196
TEN11-95-cpy (607)	0.153	0.085	0.181	2.7	0.18
TEN11-95-sph (606)	0.044	0.078	0.188	9.5	0.187
TEN2-95-born (19)	0.087	0.061	0.223	3.8	0.223
TEN2-95-born (604)	0.042	0.18	0.173	21.8	0.171
TEN11-95-py (610)	0.176	0.094	0.885	2.9	0.884
Andacollo					
Andacollo1-py (26)	0.016	6.19	6.875	3578.2	0.909
Andacollo1-py (606)	0.915	5.617	1.172	37.1	1.11
Andacollo2-py (608)	1.732	4.921	0.191	15.2	0.166
Andacollo3-py (608)	1.982	99.99	0.705	290.3	0.221
Andacollo3-py (610)	0.224	56.319	3.07	1923.3	_

Note: Measured (m) isotopic ratios are corrected back to an initial (i) ratio using a decay constant ($\lambda = 1.666 \cdot E^{-11}$ yr^{-1}) and an age of 5 Ma for El Teniente and 100 Ma for Andacollo.

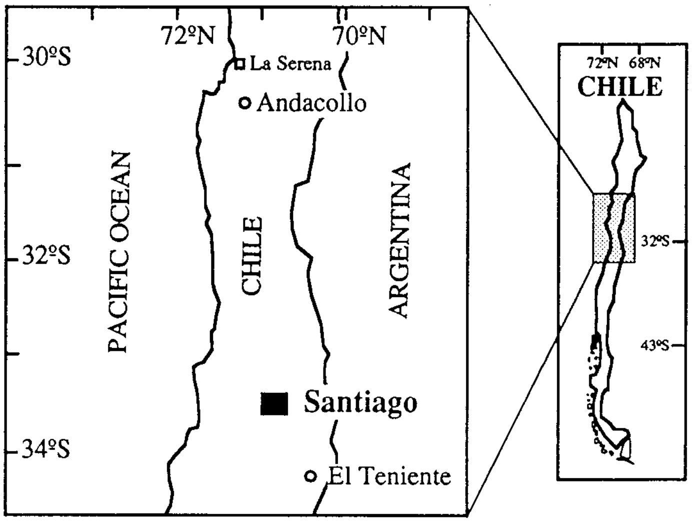

Figure 1. Location of El Teniente and Andacollo ore deposits.

leached Os from the surrounding country rocks and mixed with the magmatic fluids during the late-stage evolution of these hydrothermal systems.

At Andacollo, which is an older porphyry base metal deposit (ca. 100 Ma), five pyrite separates were used to define Re-Os isochrons. Five analyses were made on three samples (Table 1; Fig. 2B). The two separates from sample Andacollo 1 define a two-point isochron with an age of 97 Ma; the two separates of Andacollo 3, with or without a sample from Andacollo 2, yield an 89 Ma isochron; all samples define a poorly fitted isochron having an age of 103 Ma (Fig. 2B). All of these Re-Os ages are consistent with previously published K-Ar ages for sericite associated with the mineralization (Reyes, 1991). The data from Andacollo suggest that there are two methods for constructing Re-Os sulfide isochrons. The first method consists of using multiple splits from the same sample. The second method uses data from different samples that are believed to be cogenetic. The data from El Teniente indicate that because the fluids are isotopically heterogeneous during deposition, we should restrict analyses to coprecipitated minerals from a single hand sample. The data from several such hand samples can be regressed individually, yielding information on the robustness of the age and the initial isotopic ratios of the fluid(s). The Re-Os ages for all sulfides at Andacollo are robust, because the large range in ^{187}Re/^{188}Os ratios (from 15 to 3578) allows for rapid growth of ^{187}Os, and thus inhomogeneities in the fluid are insignificant. Assuming that the the initial ^{187}Os/^{188}Os isotopic ratios of the Andacollo can be extracted from two point isochrons, Andacollo has about the same range in values as El Teniente, suggesting a similar magmatic/hydrothermal evolution for the two deposits.

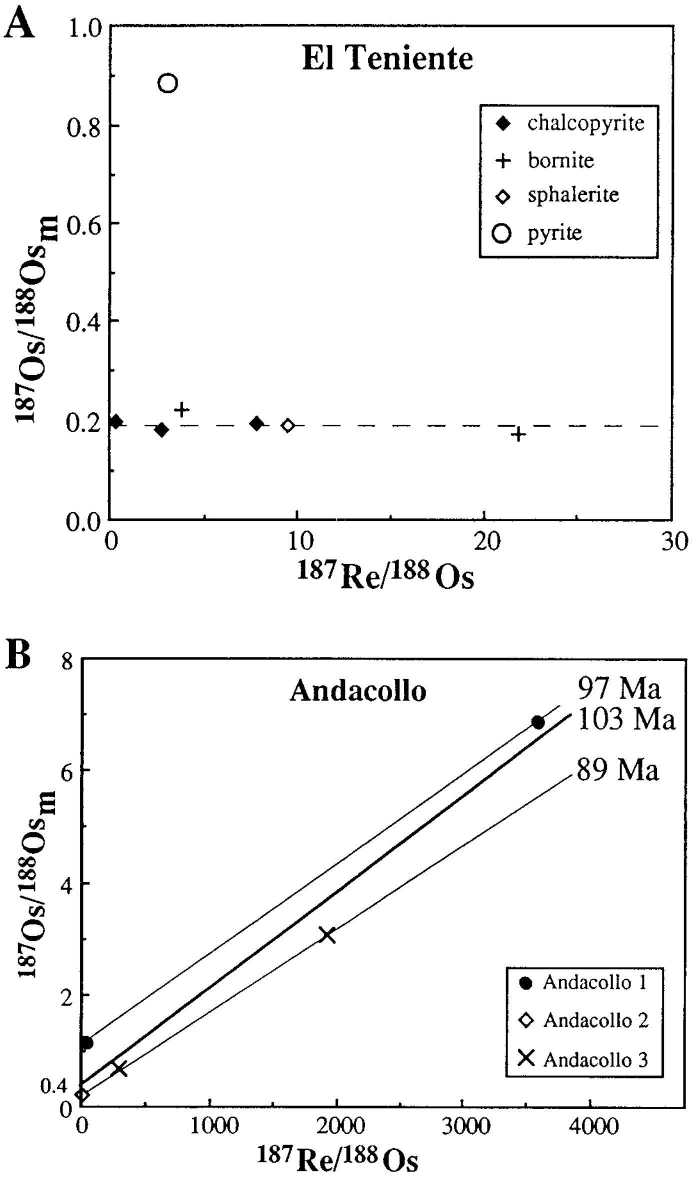

Figure 2. A: Os isochron diagram showing data for base metal sulfides from El Teniente. Dashed line represents the ^{187}Os/^{188}Os mean ratio (0.192); standard deviation is 0.017 (1σ). Analytical errors are overlapped by size of symbols. B: ^{187}Os/^{188}Os vs. ^{187}Re/^{188}Os diagram showing data for base metal sulfides from Andacollo. Analytical errors are overlapped by size of symbols.

Samples from Andacollo are more enriched in Re than those of El Teniente (Table 1) but are similar in Os concentration (0.016–2 ppb). As at El Teniente, the sulfides exhibit variable Re and Os concentrations, and pyrite separates have a very large range of ^{187}Re/^{188}Os ratios. The heterogeneities in both Re and Os concentrations may be explained by a "nugget effect," because Re and Os might be concentrated in micro-phases that are not equally distributed, or Re and Os may be from a rapidly evolving fluid, where the concentrations are continually changing as different minerals precipitate. This effect can be an advantage for determining the Re-Os geochronology of sulfides, because large variations in Re/Os ratios can be obtained from separates from the same mineral within a single hand specimen (Table 1; Fig. 2A).

CONCLUSIONS

These data show for the first time that the Re-Os isotopic method can be used to date mineralization and trace the source of Os in base metal sulfides from felsic igneous rocks. The distribution of Re and Os in sulfides does not appear to be controlled by crystallographic-chemical constraints, and therefore a single sulfide phase in a deposit can acquire vastly different Re and Os concentrations and Re/Os ratios. These characteristics, in turn, can yield very robust sulfide isochrons. The uncertainty in the obtained ages will ultimately depend on the isotopic homogeneity of the hydrothermal system from which the sulfides precipitated and the spread in Re/Os ratios of the sulfides.

In addition to determining the age of mineralization, the Re-Os isotopic system can be used to trace the source of Os and, by inference, other ore-forming metals. The initial ^{187}Os/^{188}Os isotopic ratios of sulfides from El Teniente are relatively homogeneous, indicating that the Os was largely derived from the magma, not from fluids that leached metals from the surrounding host lithologies. The evolved radiogenic isotopic character of the ore indicates that Os and, by inference, base metals in these deposits are probably derived from either a subduction-related source or subduction-related magmas mixing with a crustal component during ascent and emplacement.

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