

# Age of Mineralization of the Candelaria Fe Oxide Cu-Au Deposit and the Origin of the Chilean Iron Belt, Based on Re-Os Isotopes

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## Abstract

Re-Os isotopes are used to determine the age of iron oxide Cu-Au mineralization at Candelaria, Chile, and to explore possible genetic links with the batholithic intrusions in the area. Re-Os ages calculated from molybdenite are  $114.2 \pm 0.6$  Ma and  $115.2 \pm 0.6$  Ma, and they are interpreted to represent the age of mineralization. These ages are consistent with previously reported ages for biotite alteration that range from 114 to 116 Ma.

An isochron calculated by Re/Os ratios from hydrothermal magnetite and sulfides constrains an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of  $0.36 \pm 0.10$ . The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio for sulfide from Bronce mine, a small satellite of the Candelaria orebody, is  $0.33 \pm 0.01$ . These values are broadly similar to the calculated initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio for magmatic magnetite in nearby batholithic rocks that range from 0.20 to 0.41. The relatively radiogenic initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio represents a mixture of mantle and crustal components in the ores and batholithic rocks. The similarity in initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the ore and magmatic oxides suggest that the granitic plutons could be the source of metals in the Candelaria district. These data are consistent with the existence of a significant magmatic fluid component in the hydrothermal system as suggested by previously published work.

In order to establish a regional perspective, we analyzed ore minerals from other Chilean deposits of the iron oxide (Cu-U-Au-rare earth elements [REE]) class. Magnetite from the Manto Verde iron oxide Cu-Au deposit has Os and Re concentrations of 11 to 17 parts per trillion (ppt) and 4 to 6 parts per billion (ppb), respectively. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio is approximately 0.20 and is similar to that of ore minerals from Candelaria and of the Early Cretaceous batholithic intrusions. These data indicate a similar metal source for the mineralization at Manto Verde and Candelaria.

Magnetite from three magnetite-apatite deposits of the Chilean iron belt have Re concentrations between 0.8 and 3 ppb and Os concentrations between 11 and 76 ppt. Calculated initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios of these magnetites range from 1.2 to 8.4 and are distinctly different from those of the iron oxide Cu-Au deposits. The cause of the comparatively high radiogenic signatures in the magnetite-apatite ores is probably related to fluid interactions with (i.e., leaching) the surrounding sedimentary rocks during their genesis. In contrast to the iron oxide Cu-Au systems, the Os in magnetite-apatite ores could be derived from sedimentary rocks. This evidence suggests that predominantly basin-derived, nonmagmatic brines formed these magnetite-apatite deposits.

## Introduction

THE CANDELARIA Cu-Au deposit (470 Mt at 0.95 wt % Cu, 0.22 g/t Au, and 3.1 g/t Ag; Marschik et al., 2000) is located

about 20 km south of Copiapó, Chile (Figs. 1 and 2A). Candelaria is one of several deposits hosted in volcanic and volcanoclastic rocks that occur along the eastern margin of the Early Cretaceous Copiapó batholith. These deposits belong to a class of deposits that is characterized by abundant Ti-poor iron oxide with or without Cu, U, Au, and/or REE ores (e.g., Hitzman et al., 1992; Barton and Johnson, 1996). Genetic models that invoke immiscible melts were proposed for

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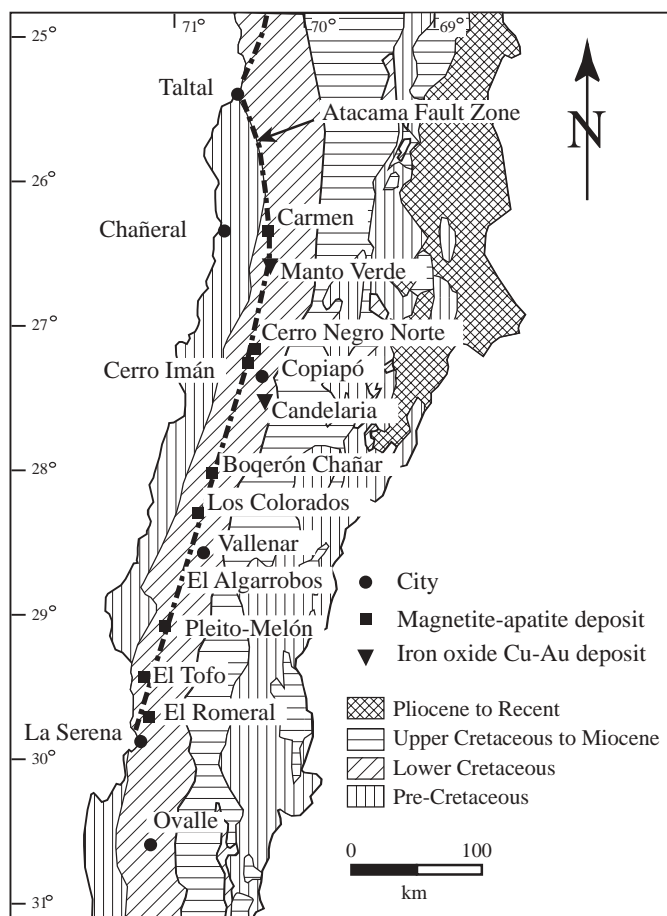


FIG. 1. Map of selected iron oxide (Cu-U-Au-REE) deposits in northern Chile.

some of the Cu-Au poor iron oxide systems such as Kiruna, Sweden (Frietsch, 1989), or the magnetite-apatite deposits of the Chilean iron belt (Nyström and Henríquez, 1994; Travissany et al., 1995). However, it is now widely accepted that these deposits formed from hydrothermal fluids (e.g., Bookstrom, 1977; Parak, 1988; Hitzman et al., 1992; Oreskes and Einaudi, 1992; Gow et al., 1994; Ménard, 1995; Vivallo et al., 1995; Marschik and Fontboté, 1996, 2001a; Ullrich and Clark, 1999; Williams et al., 1999; Requía and Fontboté, 2000; Raab et al., 2001). Characteristically, multiple hydrothermal alteration and mineralization events can be distinguished. At Candelaria, radiometric ages suggest that hydrothermal alteration and nearby pluton emplacements were contemporaneous (e.g., Zentilli 1974; Arévalo, 1994, 1995, 1999; Marschik et al., 1997a; Ullrich and Clark, 1999). Exact genetic relationships between mineralization and plutonic rocks are controversial and difficult to establish on the basis of field observations.

There are two end-member hypotheses regarding ore genesis in these systems: a magmatic-hydrothermal model and a nonmagmatic hydrothermal model (Fig. 3). The magmatic-hydrothermal model postulates that magmatic metal and sulfur-bearing fluids exsolve from a crystallizing magma (or magmas) 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 redeposit metals and sulfur (Battles and Barton, 1995; Barton and Johnson, 1996; Barton et al., 1998). Models in which both magmatic and nonmagmatic fluids are involved have been used to explain the genesis of the Candelaria orebody (Ullrich and Clark, 1999; Marschik et al., 2000; Marschik and Fontboté, 2001a).

Chilean iron oxide Cu-Au districts such as Candelaria-Punta del Cobre (e.g., Marschik and Fontboté, 1996) and Manto Verde (Vila et al., 1996) are similar in age, setting, host rocks, mineralization, and associated silicate alteration to the magnetite-apatite deposits of the Chilean iron belt (Table 1, Fig. 1). These magnetite-apatite deposits may be genetically related to Chilean iron oxide Cu-Au deposits, as implied by the work of Hitzman et al. (1992) and Barton and Johnson (1996), among others.

In this contribution, we use Re-Os isotopes to determine the age of iron oxide Cu-Au mineralization at Candelaria, to explore possible genetic links with magmatic activity in the area, and to compare magnetite-apatite deposits of the Chilean iron belt with iron oxide Cu-Au deposits. Our objectives are as follows: (1) to accurately determine the mineralization age through the use of Re-Os in molybdenite; (2) to infer possible metal sources for the iron oxide Cu-Au mineralization by comparing  $^{187}\text{Os}/^{188}\text{Os}$  initial ratios of ore minerals and magnetites from plutonic rocks; and (3) to compare Re-Os signatures of iron oxide copper-gold systems (Candelaria and Manto Verde), magnetite-apatite deposits (Romeral, Cerro Imán, Cerro Negro Norte), and Chilean porphyry copper deposits.

### Re-Os Systematics

The major advantage of using the Re-Os isotopes in ore minerals is that timing and genetic information can be obtained from the ore rather than from associated alteration minerals because Re and Os concentrate in sulfide minerals. The source of Os can be used to distinguish crustal and mantle reservoirs involved in ore formation because Re is more incompatible than Os during mantle melting (Walker et al., 1989). Crustal materials therefore have a larger Re/Os ratio and develop a higher  $^{187}\text{Os}/^{188}\text{Os}$  ratio with time compared with the mantle (Walker et al., 1989), as  $^{187}\text{Re}$  decays to  $^{187}\text{Os}$  with a half-life of about 42 Ga (Linder et al., 1989). The current chondritic mantle  $^{187}\text{Os}/^{188}\text{Os}$  ratio is approximately 0.13 (Meisel et al., 1996). Initial ratios greater than the ratios in the chondritic mantle can indicate a crustal source for Os and, by inference, for other ore forming metals. The mantle  $^{187}\text{Os}/^{188}\text{Os}$  ratio in arc environments may not be constant. Brandon et al. (1996) and McInnes et al. (1999) demonstrate that the mantle in arc environments can be metasomatized by fluids derived from a subducting slab. They found that certain portions of the mantle have  $^{187}\text{Os}/^{188}\text{Os}$  ratio measured ratios as high as 0.17.

In this study we use the source of Os in oxides and sulfides as a proxy for the source of base metals. Initial ratios greater than ratios in the chondritic mantle serve as indication of a crustal source for Os and, by inference, for other ore forming metals. Owing to their siderophile and chalcophile nature, Re and Os are assumed to behave like other base and noble metals. Wood (1987) and Xiong and Wood (2000) provide experimental

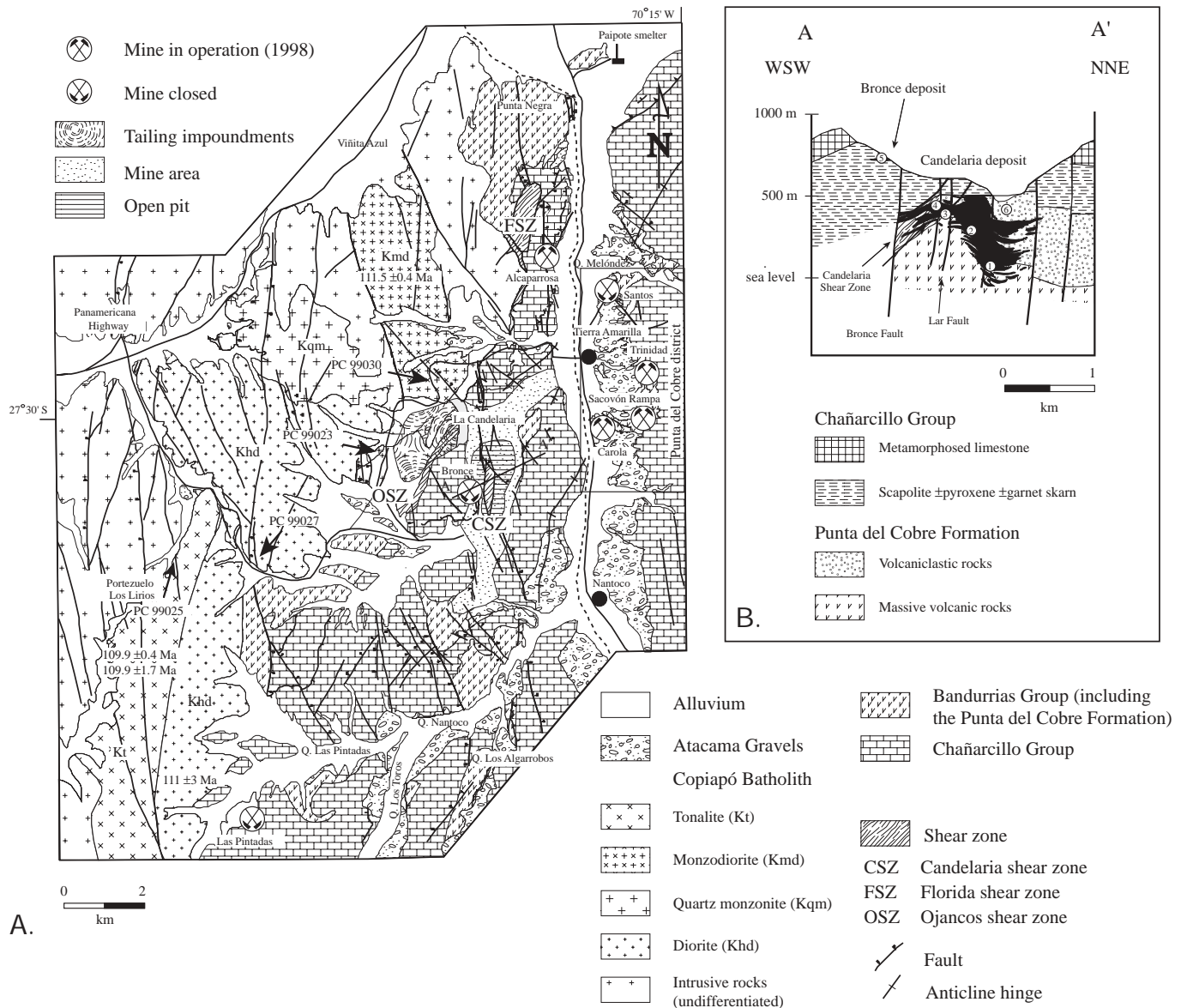


FIG. 2. A. Geologic map of the Candelaria area, modified from Tilling (1976) and Arévalo (1994, 1995). B. cross section through the Candelaria deposit. Positions of samples 1 through 6 are shown.

and theoretical evidence that documents a similar behavior of platinum group elements (PGE) in porphyry copper environments. Although there is no direct evidence that the PGE and base metals behave identically in porphyry copper systems, experimental data suggest the affinity of all metals for sulfur-rich portions of melts in magmatic systems (Mountain and Wood, 1988; Peach et al., 1990; Stone et al., 1990; Fleet et al., 1996; Sattari et al., 1998).

Molybdenite contains orders of magnitude more Re than the common sulfides and effectively no initial radiogenic  $^{187}\text{Os}$  (Luck and Allegre, 1982; Luck et al., 1983). Therefore, it can be used as a high-precision geochronometer (e.g., Herr and Merz, 1958; Hirt et al., 1963; McCandless and Ruiz, 1993; McCandless, 1994; Stein et al., 1998a, b).

## Geologic Context

The Candelaria deposit is hosted in volcanic and volcaniclastic rocks of the Early Cretaceous Punta del Cobre Formation (>1,000 m thick; Marschik and Fontboté, 2001b), which underlies marine carbonate rocks of the Chañarcillo Group (up to 2,000 m; Corvalán, 1974). These rocks represent a transition from a continental volcanic arc on the west and northwest to a shallow marine back-arc basin to the east (Fig. 2A). Marine conditions commenced in the basin in Berriasian times (about 140 Ma) and ceased owing to regional uplift in late Aptian-Albian times (about 115 Ma; e.g., Segerstrom and Parker, 1959; Jurgan, 1977; Pérez et al., 1990; UNESCO-IUGS International Stratigraphic Chart 2000).

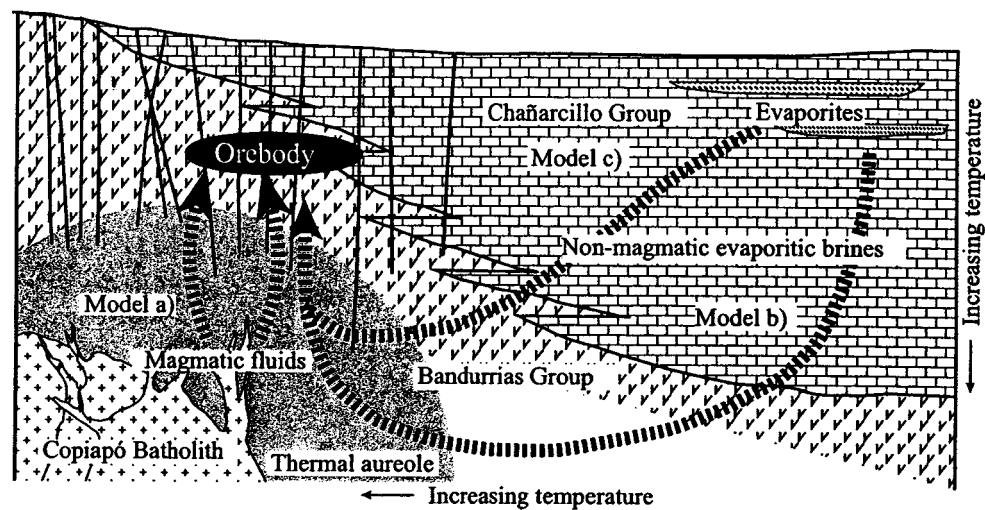


FIG. 3. End-member models for the Candelaria iron oxide Cu-Au mineralization. The Chañarcillo Group consists of limestones and shales, which presumably have relatively radiogenic Os signatures. The Bandurrias Group (including the Punta del Cobre Formation) is composed of Early Cretaceous volcanoclastic and volcanic rocks that presumably are cogenetic with the Copiapó batholith. Model a represents a magmatic-fluid-dominated system. Model b shows deep circulating evaporitic brines that acquire limestone or shale Os signatures at elevated temperatures. These fluids are not significantly modified in their Os content when they subsequently flow through the volcanoclastic rocks of the Bandurrias Group. Model c illustrates a relatively cooler fluid that does not initially acquire the Os signature of the marine back-arc deposits. However, this fluid becomes heated as it approaches the cooling plutons and leaches Os from the volcanoclastic rocks of the Bandurrias Group.

Conglomerates, andesitic lavas, and pyroclastic rocks of the Cerrillos Formation (up to 4,500 m thick) unconformably overlie the 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. 2A; Tilling, 1962, 1976). Near the Candelaria mine, the Copiapó batholith consists of several dioritic-granodioritic to quartz

TABLE 1. Characteristics of Chilean Iron Oxide (Cu-U-Au-REE) Deposits<sup>1</sup>

Characteristic	Candelaria	Manto Verde	Magnetite-apatite deposits
Geologic setting	Volcanic arc/marine back-arc environment	Volcanic arc and associated sedimentary environment	Volcanic arc and associated marine back-arc sedimentary environment
Hypogene mineralization	Magnetite-chalcopyrite-pyrite-specularite	Magnetite/specularite-chalcopyrite-pyrite	Magnetite with minor pyrite and local trace chalcopyrite
Metals	Fe, Cu, Au, Ag, Zn, light rare earth elements	Fe, Cu, Au, light rare earth elements	Fe, P
Alteration	Complex multistage superimposed potassic (K feldspar, biotite), sodic (albite, Na scapolite), calcic (Ca amphibole, epidote, diopside) alteration	Potassic (K silicate), chlorite, carbonate	Sodic (Na plagioclase, Na scapolite), calcic (actinolite, epidote, clinozoisite), apatite, carbonate
Ore controls	Northwest structures and northeast shear zone plus stratigraphic control	Major northwest structures between two branches of the Atacama fault zone	North-south structures of the Atacama fault zone
Age	115 Ma	K-Ar sericite ages of 117 ± 3 Ma and 121 ± 3 Ma	Alteration ages and ages of postore dikes range from 128 to 102 Ma
Key references	Ryan et al., 1995 Ulrich and Clark, 1999 Marschik et al., 2000	Vila et al., 1996	Zentilli, 1974 Bookstrom, 1977 Pichon, 1981 Pincheira, 1985 Espinoza, 1990 Ménard, 1995

<sup>1</sup>These deposits lie in the coastal Cordillera and occur in Early Cretaceous volcanic and volcanoclastic rocks adjacent to plutonic complexes of similar age

monzonitic intrusions. Potassium-argon ages for plutons of the batholith range from 119 to 97 Ma (e.g., Zentilli, 1974; Arévalo, 1994, 1995).  $^{40}\text{Ar}/^{39}\text{Ar}$  data from plutonic rocks in the area include a weighted mean plateau biotite age of  $111.5 \pm 0.4$  Ma (all  $^{40}\text{Ar}/^{39}\text{Ar}$  and K-Ar data are reported at  $2\sigma$  errors) for a monzodiorite (Kmd; see Fig. 2A), and a hornblende and a biotite isotope correlation age of  $109.9 \pm 1.7$  Ma and  $109.9 \pm 0.4$  Ma, respectively, for a tonalitic pluton (Kt; Arévalo, 1999).

Field relationships indicate that a hornblende diorite (Khd) predates the tonalite (Kt; Fig. 2A). The hornblende diorite (Khd) has a K-Ar biotite age of  $111 \pm 3$  Ma (Quebrada Las Pintadas), but equivalent units in the area have ages of 119 Ma (Arévalo, 1994, 1995). To the north of the tonalite outcrops, the hornblende diorite (Khd) grades into a hornblende-pyroxene diorite, which in turn has a diffuse boundary with a quartz monzonite porphyry (Kqm). The quartz monzonite porphyry (Kqm) has a distinct tectonic contact with the  $111.5 \pm 0.4$  Ma monzodiorite (Kmd) to the northeast. The diorite (Khd) and quartz monzonite porphyry (Kqm) are marginally affected by intense sodic-calcic alteration, whereas the monzodiorite (Kmd) is essentially unaffected by this type of alteration and is thought to be younger. These field relationships suggest that the diorite (Khd) is the oldest of these four plutons and for which we assume an age of 114 Ma or older. This assumed age is the older limit of the quartz monzonite porphyry (Kqm), which is consequently thought to have been emplaced between 114 and 111.5 Ma. All of these plutonic phases are potential metal, sulfur, and fluid sources for the mineralization at Candelaria and were sampled for Re-Os analysis.

### Mineralization at Candelaria and Related Deposits

Candelaria was discovered in 1987 as result of an exploration program around the Lar and Bronce mines, which hosted small manto-like sulfide copper-gold orebodies (Ryan et al., 1995). The Lar mine lay directly above the Candelaria orebody, whereas the Bronce mine is located in a different tectonic block to the east (Fig. 2B). The Bronce block is separated from the block that hosts the Candelaria ore by the north-northwest-trending Bronce fault. The Bronce and Lar mines are interpreted to represent satellites of the Candelaria orebody because of their proximity and because their ore mineralogy is similar to that at Candelaria; however, no mineralized feeder zone has been documented. Economically significant 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-sized 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).

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 (LREE), and trace quantities of molybdenite and arsenopyrite are found locally in the orebody. Copper occurs in massive veins and breccias, discontinuous veinlets or stringers, and as roughly bedding-concordant manto-like bodies. Chalcopyrite-pyrite ore 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 postmagnetite calcic amphibole alteration (e.g., Ullrich and Clark, 1999; Marschik et al., 2000; Marschik and Fontboté, 2001a).

Results from stable and radiogenic isotope studies of the ore are consistent with a predominant magmatic fluid component in the hydrothermal system. Sulfur isotope ratios of sulfides from the Candelaria deposit and several other nearby deposits fall essentially into a range of  $\delta^{34}\text{S}_{\text{CDT}}$  values between  $-3.2$  to  $+3.1$  per mil (Rabbia et al., 1996; Marschik et al., 1997a; Marschik et al., 2000). Some values of up to 7.2 per mil have been reported for sulfides from Candelaria (Ullrich and Clark, 1999) and values of 6.6 and 6.8 per mil from drill cores to the south of the Punta del Cobre (Rabbia et al., 1996). Ullrich and Clark (1999) concluded, on the basis of their paragenetic scheme and their temperature and oxygen fugacity estimates, that some of the sulfur was derived from an evaporitic source. In contrast, Rabbia et al. (1996) interpreted the small percentage (10%) of their sulfur analyses as local variations (Rabbia et al., 1996).

Oxygen isotope ratios of quartz associated with chalcopyrite from the Candelaria deposit are 11.2 to 12.6 per mil  $\delta^{18}\text{O}_{\text{SMOW}}$  (Marschik et al., 2000). Fluid inclusions in this quartz homogenize at temperatures from  $370^\circ$  to  $>440^\circ\text{C}$  (Marschik et al., 2000). The calculated isotopic fluid composition in equilibrium with quartz at these temperatures is 5.9 to  $>8.9$  per mil  $\delta^{18}\text{O}_{\text{SMOW}}$  (isotope fractionation factors of Friedman and O'Neil, 1977). These results are compatible with a fluid of magmatic origin or a nonmagmatic fluid equilibrated with silicates at high temperatures. Lead isotope compositions 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., 1997b; Marschik and Chiaradia, 2000). The data also indicate 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. None of these studies could link the mineralizing fluid to a particular intrusive phase in the area.

### Age of Alteration

Ages of silicate alteration minerals associated with iron oxide Cu-Au ore at Candelaria and surrounding deposits range from 110 to 116 Ma. The span of ages can be broken into two general periods, an older group of about 114 to 116 Ma and a younger group of 110 to 112 Ma. The most precise ages of the older group are from hydrothermal biotite. Brown biotite from the barren biotite-almandine  $\pm$  cordierite alteration at Candelaria yield an  $^{40}\text{Ar}/^{39}\text{Ar}$  weighted mean plateau age of  $116.51 \pm 0.26$  Ma (Marschik and Fontboté, 2001a). An  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau age of  $114.1 \pm 0.7$  Ma is reported Ullrich and Clark (1998, 1999) for similar brown biotite that accompanied the main magnetite formation at Candelaria. Green hydrothermal biotite from Candelaria that is associated with chalcopyrite-pyrite gave an  $^{40}\text{Ar}/^{39}\text{Ar}$  weighted mean plateau age of  $115.14 \pm 0.18$  Ma (Marschik and Fontboté, 2001a). This biotite age is identical with an  $^{40}\text{Ar}/^{39}\text{Ar}$  inverse isochron

age of  $114.9 \pm 1.0$  Ma for ore-related green hydrothermal biotite from Santos mine (Punta del Cobre district; Marschik et al., 1997a). A less precise  $^{40}\text{Ar}/^{39}\text{Ar}$  total fusion age of  $114.6 \pm 1.6$  Ma for green biotite from the Resguardo mine (Punta del Cobre district), and a Rb-Sr isochron age of  $116.8 \pm 2.7$  Ma calculated from data of seven potassium metasomatized whole-rock samples (Marschik et al., 1997a) are consistent with the previous biotite ages. Euhedral amphibole in massive chalcopyrite-pyrrhotite from Candelaria has a somewhat disturbed age spectrum. A pseudoplateau age calculated from five consecutive steps with similar K/Ca ratios and comparable radiogenic yield, and which contain 52 percent of gas released, is  $116.6 \pm 1.2$  Ma (Marschik and Fontboté, 2001a).

Ages that fall in the younger group of 110 to 112 Ma include an  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau age of  $111.7 \pm 0.8$  Ma for hydrothermal amphibole associated with chalcopyrite from Candelaria (Ullrich and Clark, 1999). According to Ullrich and Clark (1999), this amphibole age represents the age of the Cu-Au mineralization. An  $^{40}\text{Ar}/^{39}\text{Ar}$  correlation age of  $110.7 \pm 1.6$  Ma for biotite from Candelaria (Arévalo, 1999) and an  $^{40}\text{Ar}/^{39}\text{Ar}$  total fusion weighted mean age of  $111.6 \pm 1.4$  Ma (two analyses) for ore-related green biotite from the Resguardo mine are identical with the younger amphibole age mentioned above.

## Samples and Analytical Techniques

Hydrothermal magnetite, chalcopyrite, and pyrite from Candelaria and pyrite from Bronce mine were chosen for Re-Os analyses. Samples were taken from drill cores and benches in these mines. They represent the main phase of mineralization. Sample locations relative to the stratigraphy are shown in Figure 2B. Sample descriptions are given in Table 2.

The samples were wrapped in paper, crushed, and sieved. Magnetic separations provided pure samples of each phase. Diorite (Khd), quartz monzonite porphyry (Kqm), monzodiorite (Kmd), and tonalite (Kt) samples (locations labeled in Fig. 2B) were crushed and sieved, and the magnetic fraction was separated for analyses. These plutonic rock samples do not contain hydrothermal or magmatic sulfides and represent the least-altered rocks found in the area. Mineral separates of magnetites from the intrusive rocks were used because the bulk of Re and Os probably reside in the magmatic sulfides associated with the magnetite or in the magnetite itself (Righter et al., 1998). High-grade magnetite ore from selected magnetite-apatite deposits of the Chilean iron belt and massive magnetite from a drill core of Manto Verde were ground and separated magnetically from minor silicate alteration minerals to obtain pure magnetite concentrates.

TABLE 2. Sample Locations and Descriptions

Sample	Sample source	Location number in Fig. 2	Description	Ore mineral
Candelaria moly-1, 2	Candelaria North pit Bench 416	6	Amphibole-andradite-magnetite skarn with veinlets of chalcopyrite-pyrite, and molybdenite in veinlets and as disseminations	Molybdenite
Cand-1	Candelaria North pit	1	Core sample from foliated biotitized meta-andesites, cpy + py, anhydrite veinlets, spots of epidote and potassic feldspar, disseminations of amphibole and sphene	Chalcopyrite
Cand-2	Candelaria North pit	2	Core sample from dark green andesitic rocks with chalcopyrite-pyrite and minor magnetite, pervasive biotite, quartz, K feldspar, and amphibole veinlets, traces of epidote	Chalcopyrite
Cand-3a, b	Candelaria North pit	3	Core sample from originally volcanoclastic rock with intense pervasive magnetite-amphibole alteration and chalcopyrite-pyrrhotite	Magnetite
Cand-4	Candelaria South pit	4	Sample from the upper part of the magnetite-amphibole-chalcopyrite-pyrite body	Chalcopyrite
Bronce-3	Bronce mine	5	Sample from the central portion of the stratiform chalcopyrite-pyrite body, pervasive sodic scapolite alteration	Pyrite
PC 99023	West of Candelaria tailing impoundments		Quartz monzonite porphyry (Kqm)	Magnetite
PC 99025	North of Portezuelo Los Lirios		Granodiorite-tonalite (Kt)	Magnetite
PC 99027	Road between Candelaria and Panamerican highway		Hornblende diorite (Khd)	Magnetite
PC 99030	Roadcut between Tierra Amarilla and Candelaria		Monzodiorite (Kmd)	Magnetite
Cerro Negro Norte	Central part of the open cut		High-grade magnetite ore	Magnetite
Cerro Imán	Open pit		High-grade magnetite ore	Magnetite
El Romeral	Central part of pit		High-grade magnetite ore	Magnetite
Manto Verde			Core sample from massive magnetite-pyrite-chalcopyrite ore with minor calcite	Magnetite

Molybdenite was hand-picked from an amphibole-rich samples that were collected from bench 416 in the northern part of the Candelaria pit. We evaluated the quality of this molybdenite using electron microprobe analysis as suggested by McCandless (1994). Molybdenite ages can be calculated by two methods: by using a conventional isochron plot with the concentration of daughter  $^{187}\text{Os}$  vs. parent  $^{187}\text{Re}$  (Stein et al., 1998 a), or by assuming no initial radiogenic  $^{187}\text{Os}$  (i.e.,  $^{187}\text{Os}_m = ^{187}\text{Re}_m(e^{\lambda t} - 1)$ ;  $m$  = measured,  $\lambda$  = decay constant,  $t$  = time). The decay constant we used for Re is  $1.66 \times 10^{-11} \text{ yr}^{-1}$  (Smoliar et al., 1996).

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 to those described in Mathur (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 than the normal 3:1 mixture. Sample preparation and loading techniques are from Creaser et al. (1991).

### Results

The molybdenite samples yield mineralization ages of  $114.2 \pm 0.6 \text{ Ma}$  and  $115.2 \pm 0.6 \text{ Ma}$ . These ages were calculated assuming no initial  $^{187}\text{Os}$ , and we obtained concordant results applying the isochron method. The combined error associated with a variable blank contribution and the weight of

sample and spike is less than the error of the concentration of Re and Os in the spikes ( $\pm 0.5\%$ ). Therefore, the reported errors of the molybdenite ages account for the greatest source of error in the analysis, which is the error associated with the concentration of Re and Os in the spike.

McCandless (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 lack of clay overgrowths on the molybdenites at the microprobe level and the reproducible age derived by this study indicate that they (the molybdenites) most likely reflect the age of mineralization rather than alteration ages.

Hydrothermal magnetite, chalcopyrite, and pyrite from the Candelaria orebody have concentrations of Os and Re of 9 to 23 ppt (parts per trillion) and 0.4 to 4 ppb (parts per billion) respectively (Table 3). Hydrothermal magnetite from Manto Verde has 11 to 17 ppt Os and 4 to 6 ppb Re. Hydrothermal magnetites from the iron belt deposits have Os concentrations of 11 to 71 ppt and Re concentrations of 0.8 to 10 ppb.

Internal reproducibility for the measurements is always better than 0.2 percent ( $2\sigma$ ); however, this value underestimates the error of the analysis because of the variable contribution of Os from the procedural blanks. Whole procedure chemical blanks during this study contributed 1.5 to 2.7 picograms of Os and 25 to 35 picograms of Re. Because the greatest source of error in the analysis is the Os concentration in the Os blank, errors for the magnetites and sulfides are calculated by varying the blank concentration. The  $^{187}\text{Os}/^{188}\text{Os}$

TABLE 3. Re-Os Results

Sample	Phase	Re (ppt) <sup>1</sup>	Os (ppt) <sup>1</sup>	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}_i$	Age
<b>Candelaria</b>							
Candelaria moly-1	Molybdenite	73.11 ppm	85.31 ppb				$115.2 \pm 0.6$
Candelaria moly-2	Molybdenite	77.21 ppm	93.47 ppb				$114.2 \pm 0.6$
Cand-1	Chalcopyrite <sup>2</sup>	4,874	19	$1,702 \pm 135$	$3.12 \pm 0.28$	$0.36 \pm 0.10$	$110 \pm 9$
Cand-2	Chalcopyrite <sup>2</sup>	1,592	13	$739 \pm 51$	$1.77 \pm 0.12$	$0.36 \pm 0.10$	$110 \pm 9$
Cand-2	Magnetite	3,059	17	$1,235 \pm 86$	$2.61 \pm 0.21$	$0.36 \pm 0.10$	$110 \pm 9$
Cand-3a	Magnetite <sup>2</sup>	428	9	$298 \pm 31$	$0.91 \pm 0.09$	$0.36 \pm 0.10$	$110 \pm 9$
Cand-3b	Magnetite <sup>2</sup>	335	6	$242 \pm 36$	$0.80 \pm 0.10$	$0.36 \pm 0.10$	$110 \pm 9$
Cand-4	Chalcopyrite <sup>2</sup>	4,896	23	$1,516 \pm 144$	$3.32 \pm 0.30$	$0.36 \pm 0.10$	$110 \pm 9$
<b>Bronce</b>							
Bronce- 3	Pyrite				$0.45 \pm 0.001$		
Bronce- 3	Pyrite				$0.45 \pm 0.001$		
Bronce- 3	Pyrite	16,326	1326	$61 \pm 0.61$	$0.45 \pm 0.001$	$0.33 \pm 0.01$	
<b>PC</b>							
PC 99023 Kap	Magnetite	4,059	209	$96 \pm 1$	$0.38 \pm 0.01$	$0.21 \pm 0.01$	
PC 99025 Kt	Magnetite	849	43	$102 \pm 5$	$0.61 \pm 0.01$	$0.41 \pm 0.01$	
PC 99027 Khd	Magnetite	2,517	60	$214 \pm 5$	$0.65 \pm 0.01$	$0.24 \pm 0.01$	
PC 99030 Kmd	Magnetite	3,281	76	$229 \pm 9$	$0.69 \pm 0.02$	$0.27 \pm 0.02$	
Cerro Negro Norte	Magnetite	882	76	$103 \pm 9$	$7.72 \pm 0.7$	$7.59 \pm 0.72$	
Cerro Imán	Magnetite	804	38	$135 \pm 20$	$2.36 \pm 0.2$	$2.16 \pm 0.21$	
El Romeral	Magnetite	3,439	11	$2,881 \pm 690$	$7.01 \pm 1.6$	$1.50 \pm 0.30$	
Manto Verde	Magnetite	6,032	17	$2,934 \pm 449$	$5.86 \pm 0.87$	$0.20 \pm 0.05$	
Manto Verde	Magnetite	4,175	11	$3,541 \pm 1400$	$7.02 \pm 2.7$	$0.20 \pm 0.05$	

Concentrations, isotope ratios, initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios, and ages of the phases analyzed; Os concentrations for molybdenite are total  $^{187}\text{Os}$ ; reported molybdenite ages assume no initial  $^{187}\text{Os}$ ; errors of the ages take the accuracy of the determination of the Re spike concentration into account; ages used to calculate initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio for the plutonic rocks are as follows: tonalite (Kt) = 110 Ma, monzodiorite (Kmd) = 111.5 Ma, hornblende diorite (Khd) = 114 Ma, and quartz monzodiorite porphyry (Kqm) = 113 Ma; age used to calculate initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio for the magnetite from the magnetite-apatite deposits is 115 Ma; errors for the  $^{187}\text{Re}/^{188}\text{Os}$  ratio and  $^{187}\text{Os}/^{188}\text{Os}$  ratios assume the greatest possible deviation and were calculated by varying the concentration of the Os blank (1.5–2.7 picograms, as discussed in the text)

<sup>1</sup>Unless specified otherwise in table

<sup>2</sup>May contain traces of pyrite (<5 percent)



ratio of the blank remained constant ( $0.175 \pm 0.008$ ). The calculated errors are listed in Table 3 and represent a deviation of the mean owing to the variable contribution of the blank. Age and initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio ratios were calculated with the program MACDAT-2, written by C. Isachsen and D. Coleman (University of Arizona) using the algorithms of York (1969).

The isotopic ratios from hydrothermal ore minerals form an isochron with an age of  $110 \pm 9$  Ma (mean square of weighted deviates, 1.4) with an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of  $0.36 \pm 0.10$  (Fig. 4). The samples from Bronce mine have more Os (about 1 ppb) and Re (16 ppb) compared with the Candelaria ore minerals. The two analyses from Manto Verde form a trend on an isochron plot that suggests an age of 116 Ma. This age is similar to K-Ar sericite ages of  $117 \pm 3$  Ma and  $121 \pm 3$  Ma for the deposit (Vila et al., 1996), and it was used to calculate the initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio. K-Ar ages of alteration minerals and postore dikes in the magnetite-apatite deposits of the iron belt are between 128 Ma and 102 Ma (Zentilli, 1974; Pichon, 1981). These ages are interpreted to roughly constrain the age of mineralization. We assume an average mineralization age of 115 Ma for these deposits to calculate the initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios do not change significantly (not greater than  $\pm 0.5$  of the initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio) when calculated using mineralization ages of 128 Ma or 102 Ma.

The magmatic magnetites from the Copiapó batholith contain 40 to 200 ppt Os and 0.8 to 4 ppb Re. Initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios calculated for these magnetites range from 0.2 to 0.4. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios were calculated by using  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of Arévalo (1999) for the corresponding intrusions: tonalite (Kt; 109.9 Ma) and monzodiorite (Kmd; 111.5 Ma). Field relationships indicate that the tonalite (Kt) and the quartz monzonite porphyry (Kqm) are younger than the hornblende diorite (Kmd), and therefore an age of 113 Ma was assumed for quartz monzonite porphyry (Kqm).

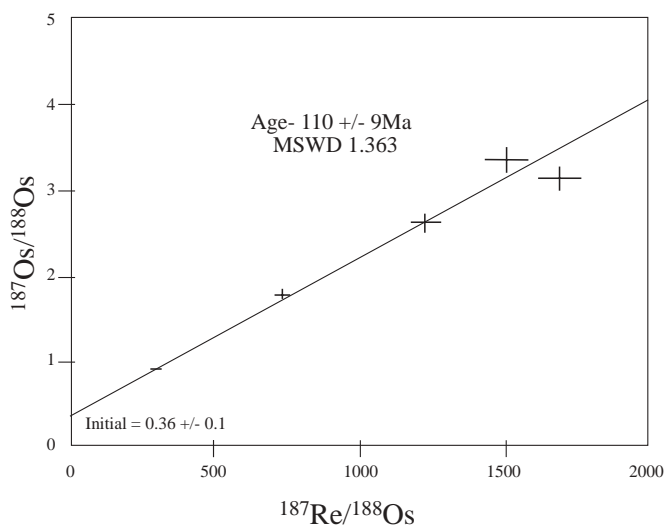


FIG. 4. Isochron plot of the hydrothermal magnetite, chalcopyrite, and pyrite from the Candelaria mine. Statistical analysis of the fitting of the curve is derived from algorithms similar to those of York (1969).

## Discussion

The Re-Os molybdenite ages of  $114.2 \pm 0.6$  Ma and  $115.2 \pm 0.6$  Ma are interpreted to represent the age of the Cu-Au mineralization at Candelaria, because formation of molybdenite overlapped the main copper mineralization (Fig. 5; Ullrich and Clark, 1999; Marschik and Fontboté, 2001a). These ages are consistent with alteration ages between 114 and 116 Ma previously reported from Candelaria and similar deposits in the nearby Punta del Cobre district (Marschik et al., 1997b; Ullrich and Clark, 1999; Marschik and Fontboté, 2001a). The age data suggest that the amphibole age of  $111.7 \pm 0.8$  Ma and the other younger alteration ages of 110 to 112 Ma could record a younger mineralization and/or hydrothermal event (Marschik et al., 1997b; Marschik and Fontboté, 2001a). The quartz monzodiorite (Kmd; 111.5 Ma) and the tonalite (Kt; 109.9 Ma) could have caused this thermal (or hydrothermal) event (Fig. 2A). The Re-Os isochron age of  $110 \pm 9$  Ma derived from hydrothermal magnetite, chalcopyrite, and pyrite has an error that spans the range of previous radiometric ages and is unsuitable for determining a mineralization age.

The radiometric ages indicate that mineralization at Candelaria is closely coupled with the cooling and crystallization of the nearby intermediate plutonic rocks. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio for magmatic and hydrothermal magnetite, chalcopyrite, and pyrite is around 0.3, and it reveals that there is a relatively large crustal component in the magma and the ores (Fig. 6). Possible radiogenic sources for Os in magmas that occur in arc or back-arc environments are the upper or lower continental crust (which was relatively thin at this time), the subducting slab and its accompanying sedimentary rocks, and/or a metasomatized mantle (Esser and Turekian, 1993; Brandon et al., 1996; Roy-Barman et al., 1997).

Figure 6 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 similarity indicates that the source of Os in the batholith magmas, the main orebody, and its satellite are similar. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios of the ore ( $0.36 \pm 0.10$ ) overlap with the ratio of the diorite ( $0.25 \pm 0.01$ ). In addition, the averaged molybdenite age of 114.7 Ma is similar to the assumed age of  $\geq 114$  Ma of the diorite (Khd; Fig. 2A). These results indicate that mineralization could be genetically related to the earlier dioritic phases of the Copiapó batholith.

This Re-Os evidence for a magmatic origin of the ores is consistent with other isotopic data, such as (1) oxygen isotope

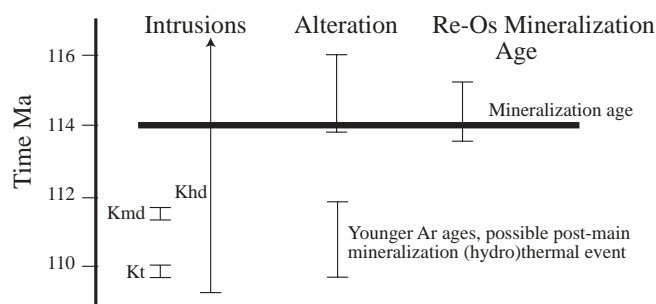


FIG. 5. Geochronological data on ore minerals, alteration, and the batholithic rocks from the Candelaria district.



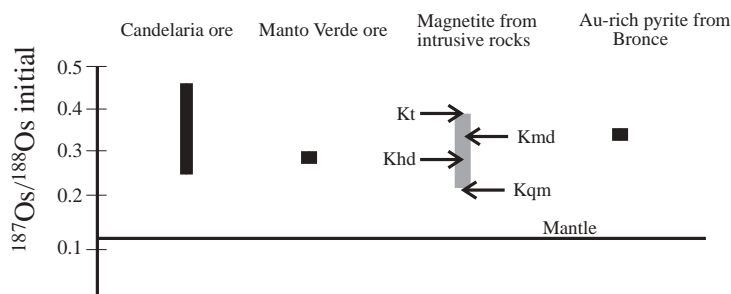


FIG. 6. Comparison of the calculated initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios. Note the overlap of all the initial ratios.

data and microthermometric data, which are compatible with a significant magmatic fluid component in the hydrothermal system during the main copper mineralization; (2) the overlapping lead isotope signatures of ore minerals from Candelaria and the Punta del Cobre district and plutonic rocks of the Copiapó batholith; and (3) the sulfur isotope ratios of most of the sulfides from Candelaria and other related deposits, which are near 0 per mil  $\delta^{34}\text{S}_{\text{CDT}}$ .

In order to explore further the evidence for a predominantly magmatic or nonmagmatic fluid component 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  $^{187}\text{Os}/^{188}\text{Os}$  isotope ratio of the magmatic fluids and the fluids derived from sedimentary rocks is difficult. The main problem is estimating the Os concentration of the basinal brines and magmatic fluids.

There is evidence that Os is mobile in solutions similar to those that formed Candelaria. Suzuki et al. (2000) showed that Re and Os are mobile in typical lower-temperature hydrothermal solutions because they could isotopically alter molybdenite in saline solutions (i.e., 0.1N 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 and river waters with time (Sharma et al., 1997; Puecker-Ehrenbrink and Blum, 1998), although the concentration Os in the water is very dilute (at femtogram levels).

A basinal brine during Candelaria's genesis would have had a temperature of about 120°C and would have been capable of acquiring the Os isotope signature of the surrounding sedimentary rocks. The depth of mineralization at Candelaria was less than 3 km. The Candelaria orebody is hosted in the upper part of the Punta del Cobre Formation, which is overlain by up to 2,000 m of limestones of the Chañarcillo Group. The Chañarcillo Group was uplifted and partially eroded in late Aptian times, i.e., at the time of mineralization. Consequently, the depth of mineralization is equal to the thickness of the Chañarcillo Group plus the thickness of the part of the Punta del Cobre Formation that overlies the orebody. A hypothetical evaporite-derived brine would probably have a temperature of >120°C assuming that this fluid penetrated to a depth of 3 km. This basin probably had a minimum geothermal gradient of 40°C/km (model b in Fig. 3). This fluid would possibly acquire an Os isotope signature close to that of the penetrated sedimentary rocks. Shales, mudstones, and limestones have radiogenic signatures and typically have Os

concentrations that exceed 100 ppt (Raivizza and Turekian, 1989; Esser and Turekian, 1993; Raivizza, 1993; Sign et al., 1999; Chesley et al., 2000). This value is a conservative estimate, because saline fluids can contain more than 1 ppb Os (Xiong and Wood, 2000).

Determining the Os isotope ratio in this basinal brine is also difficult. The initial isotopic value of the limestones, evaporites, shales, and mudstones from which the brine could have originated are in the range of 135 Ma to 115 Ma. At the time of their deposition, these marine sediments probably had an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio resembling that of seawater, which was about 0.8 as established by Cohen et al. (1999). Assuming this initial ratio and a modest Re/Os ratio of about 250 for marine sedimentary rocks (Cohen et al., 1999) at the time of ore deposition (about 114–115 Ma), the sedimentary rocks would have a measured  $^{187}\text{Os}/^{188}\text{Os}$  ratio of about 1. If the fluid was in isotopic equilibrium with the sediments, the Os isotope ratio would be 1 and should therefore be detectable in the ores.

Although there is evidence for mobility of Os in hydrothermal solutions that were involved in the genesis of Candelaria, our data are consistent with a dominantly magmatic fluid component in 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 en route to the cooling intrusion (model b in Fig. 3). Once close to the heat source, the brine may acquire Os from the volcanoclastic rocks of the Bandurrias Group, which 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 lies in 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 represent of a zonation 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, and there might be Cu/Au fractionation at district scale. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of Bronce ore is similar to that of Candelaria and those of the granitoid rocks, thus indicating essentially the same source. This finding is the opposite of that at Grasberg, where a clear mixing relationship existed between magmatic and sedimentary sources in the peripheral parts of the hydrothermal system (Mathur et al., 2000b). Perhaps the correspondence between the peripheral ores and magmas provides stronger evidence for a magmatic source.

Cu-Au deposits and magnetite-apatite deposits may be genetically related (Hitzman et al., 1992; Barton and Johnson, 1996). Marschik and Fontboté (1996) genetically interpreted the iron oxide Cu-Au mineralization at Candelaria-Punta del Cobre to occupy a transitional position between the magnetite (-apatite) ores of the Chilean iron belt and Andean porphyry copper deposits. Figure 7A, B explores relationships between these deposits by comparing the Re-Os concentrations and  $^{187}\text{Os}/^{188}\text{Os}$  initial ratios of ore minerals from Chilean iron oxide Cu-Au (Candelaria and Manto Verde), magnetite-apatite (El Romeral, Cerro Imán, and Cerro Negro Norte deposits), and porphyry copper deposits (Mathur, 2000; Mathur et al., 2000a).

In terms of total Re and Os concentration, there are no marked differences between the iron oxide Cu-Au deposits and the magnetite-apatite and porphyry copper systems (Fig. 7A). Re concentrations in magnetite-apatite deposits are relatively uniform compared with those of porphyry copper and iron oxide Cu-Au systems. Sulfides from porphyry copper deposits usually have Os concentrations less than 30 ppt, whereas magnetite from the magnetite-apatite deposits may contain significantly higher Os concentrations. It is important to note that elevated Os concentrations are detected in

peripheral parts of iron oxide Cu-Au systems as shown by the data from the Bronze mine.

There is a distinct difference in the initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio between the iron oxide Cu-Au and magnetite-apatite deposits (Fig. 7B). Ore minerals from the magnetite-apatite deposits have more radiogenic signatures than those of the iron oxide Cu-Au deposits. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio from the magnetite-apatite deposits is also distinctively different from those of the plutonic rocks near Candelaria. This difference indicates that the magnetite-apatite ores acquired their radiogenic  $^{187}\text{Os}$  signatures from a highly time-integrated source that does not resemble the plutonic rocks near Candelaria.

The hypothetical fluid and metal sources discussed above for Candelaria (Fig. 3) are also valid for the magnetite-apatite deposits of the Chilean iron belt. As previously mentioned, a basinal brine that interacted with and acquired metals from sedimentary rocks of the Chañarcillo Group would have an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of around 1. This signature, which was not detected in the Candelaria or Manto Verde ores, is found in the magnetite-apatite ores. Therefore, initial  $^{187}\text{Os}/^{188}\text{Os}$  compositions of the magnetite-apatite ores could be interpreted as evidence for the involvement of a basinal brine that acquired a sedimentary signature shown in model b of Figure

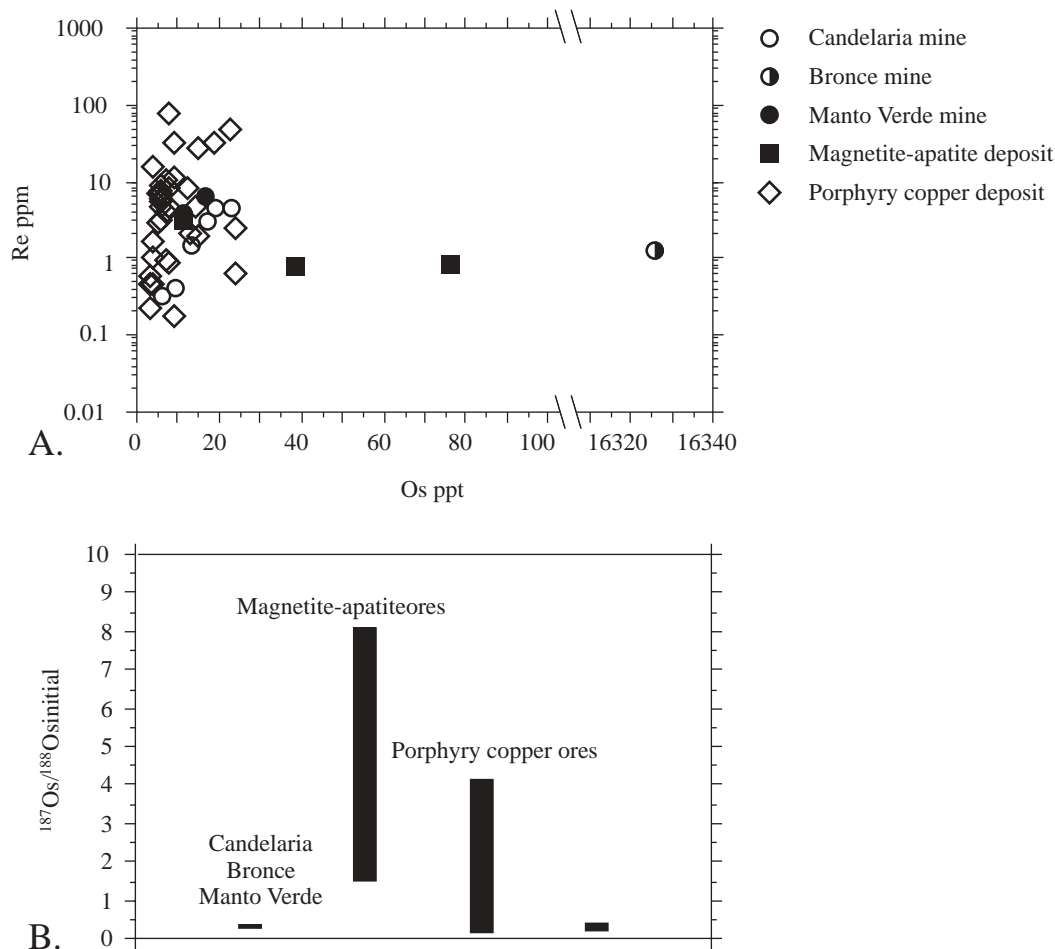


FIG. 7. A. Re and Os concentrations of ores from Chilean iron oxide (Cu-U-Au-REE) and porphyry copper deposits. B. Comparison of initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios of ores from Chilean iron oxide (Cu-U-Au-REE) systems, porphyry copper deposits, and batholithic rocks near Candelaria.

3. The initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of Chilean porphyry copper ores overlap with both iron oxide Cu-Au and magnetite-apatite ores.

### Conclusions

Re-Os ages from molybdenite of 114.2 to 115.2 Ma represent the age of Cu-Au mineralization at Candelaria. These ages are consistent with previously reported ages between 114 and 116 Ma for hydrothermal alteration at Candelaria and similar deposits in the nearby Punta del Cobre district. The isochron age of  $110 \pm 9$  Ma derived from hydrothermal magnetite, chalcopyrite, and pyrite is identical within error with the Re-Os molybdenite and the alteration ages of the district.

Calculated initial  $^{187}\text{Os}/^{188}\text{Os}$  values have important petrologic and metallogenic information. Initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio of magmatic magnetite from the granitoid plutons of the Copiapó batholith range from 0.20 to 0.41. This ratio implies that these magmas have mantle and crustal components. Initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios from hydrothermal magnetite, chalcopyrite, and pyrite from Candelaria and Bronce are 0.26 to 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 are compatible with the hypothesis that predominately magmatic fluids caused the main mineralization at Candelaria, but they do not exclude alternative models that invoke nonmagmatic fluids.

Comparatively high radiogenic signatures found in the magnetite-apatite ores indicates the involvement of a different source of Os (and by inference the base metals) than seen at Candelaria and Manto Verde. This apparent difference in the Os isotope composition of the ores could be linked with their genesis. The results from the magnetite-apatite orebodies could indicate that basin-derived, nonmagmatic, ore-forming brines are responsible for the formation of the magnetite-apatite deposits of the Chilean iron belt, whereas Candelaria and Manto Verde have a stronger magmatic signature.

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