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Review Article

Genetic Aspects of the Manto-type Copper Deposits Based on Geochemical Studies of North Chilean Deposits

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Abstract

Recent studies on mineralogy, geochronology, fluid inclusion and stable isotope (Pb, Os, S, C, O, Sr) characteristics were reviewed to determine constraints for genetic models of the Chilean manto-type copper deposits. The Chilean manto-type deposits are divided into the two geologic categories of the northern areas (Arica–Iquique, Tocopilla–Taltal) and the central areas (Copiapó, La Serena, Santiago). The former is distributed in the coastal range composed of Jurassic andesite-dominated volcano-sedimentary piles and younger plutonic intrusions, and yields chalcocite (-digenite) and bornite as the principal hypogene copper sulfides. The latter is hosted mostly in Lower Cretaceous volcano-sedimentary sequences, and has chalcopyrite-rich mineral associations. The fluid inclusion data indicate that the primary copper mineralization was commonly generated in the temperature range 150–360°C under low-pressure conditions near the boiling curve, mediated with relatively saline brines. Generally, homogeneous Pb and S isotope compositions for primary copper minerals imply direct magma source or leaching of igneous rocks. Pb and Os isotope data published for some deposits, however, suggest that ore-forming metals were derived mainly from the volcano-sedimentary host rocks. The noticeably negative isotope ratios of primary sulfide sulfur and hydrothermal calcite carbon of some central area deposits indicate influx of sedimentary rock components, and the high $^{87}Sr/^{86}Sr$ initial ratios of hydrothermal calcite from the Tocopilla–Taltal area deposits imply contribution of the contemporaneous seawater or marine carbonates. These isotopic constraints imply a formation mechanism in which the Chilean manto-type copper deposits formed epigenetically in the process of hydrothermal interaction of non-magmatic surface-derived brine with the volcano-sedimentary host rocks, which is inferred to have been induced by a deep-seated plutonic complex as the possible heat source.

Keywords: Chilean manto-type deposits, coastal Cordillera, hydrothermal fluid–rock interaction, isotope geochemistry, primary copper sulfides, volcano-sedimentary piles.

1. Introduction

In the Coastal Cordillera of Northern Chile (north of Santiago, <34°S), numbers of volcanic-hosted stratabound copper deposits termed "manto-type" are distributed (Ruiz *et al.*, 1965; Camus, 1990), forming an economically important cupriferous metallogenic belt in Chile. Similar type of deposits in North America are named "volcanic redbed" (Kirkham, 1996; Lefebure & Church, 1996; Cabral & Beaudoin, 2007), and are distributed principally in the northwest Canada and north Michigan district (e.g. White, 1968; Wilton & Sinclair, 1988). Most of the aforementioned deposits occur in andesitic to basaltic rock-dominated

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volcano-sedimentary piles of Mesozoic age (Chile) and much older Proterozoic to Triassic age (North America). Unfortunately, the currently operating mines producing significant copper are almost only in Northern Chile. Thus, a variety of geological information has been accumulated solely on Chilean manto-type copper deposits, which are an important object of mineral exploration (Yoshizawa *et al.*, 2003). In particular, studies on geochronology, fluid inclusions and stable isotopes have greatly progressed, and enable us to discuss ore-forming conditions and origin of ore-forming elements. Despite such a context, most studies are limited in local metallogeny, and an effort to inclusively model the manto-type ore formation has not yet been made. In this aspect, a genetic model of the manto-type deposits still remains in question, as compared with Chilean porphyry copper deposits. The present study attempts to establish a uniformly explainable formation model for the Chilean manto-type copper deposits, based on recent geological information, particularly on a variety of isotope data, to determine constraints for the origin of ore-forming elements.

2. General geology of ore deposits

Principal manto-type copper deposits in Northern Chile are divided into the following five areas: Arica–Iquique, Tocopilla–Taltal, Copiapó, La Serena and Santiago (Fig. 1). Most deposits of the areas occur in Jurassic–Lower Cretaceous volcano-sedimentary sequences, and their geologic characteristics have been summarized in review article by Sato (1984). The deposits of the northern areas (Arica–Iquique and Tocopilla–Taltal) are located in a lateral belt along the coastal range, in contrast to those of the central areas (Copiapó, La Serena, Santiago) distributed in the intracontinental back-arc basins (e.g. Camus, 1990; Sillitoe, 2003). Furthermore, some geological differences are recognized between the two groups, as indicated by Sato (1984): the northern area deposits are hosted in basaltic andesite to andesite-dominated Jurassic volcanic-sedimentary piles (Camaraca, Ofícina Viz and La Negra Formations), except the Mantos Blancos deposit, which is hosted in the Jurassic felsic volcanics and subvolcanic intrusions (Cornejo *et al.*, 2006; Ramírez *et al.*, 2006). In contrast, the central area deposits occur in Lower Cretaceous (mainly Neocomian) volcano-sedimentary sequences including considerable amounts of sandstone, tuffaceous siltstone and limestone (Table 1). This difference is reflected in the primary mineraliza-

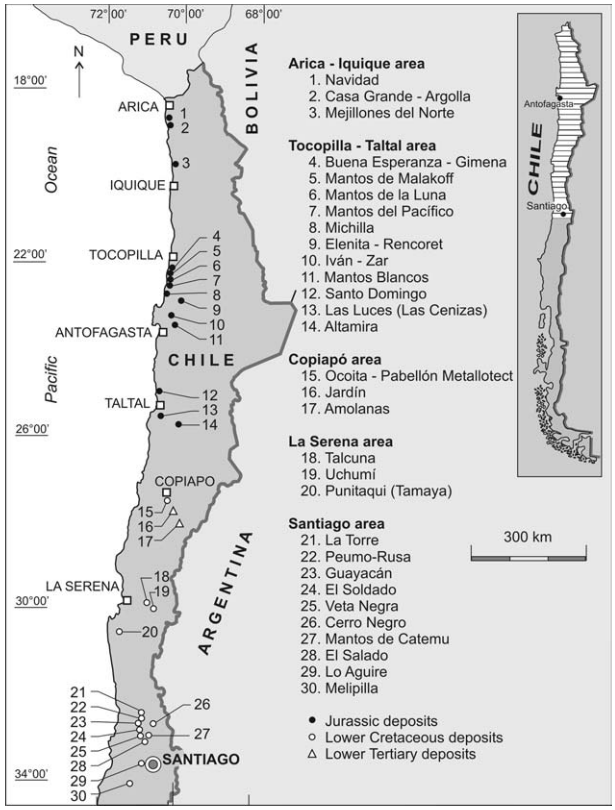

Fig. 1 Spatial distribution of principal manto-type copper deposits in northern Chile (compiled from Sato, 1984; Camus, 1990; Maksaev *et al.*, 2007).

tion ages ranging from Early Upper Jurassic to Late Lower Cretaceous (*ca* 100 Ma to *ca* 160 Ma; e.g. Wilson *et al.*, 2003a; Tristá-Aguilera *et al.*, 2006). Exceptionally, the Jardín and Amolanas deposits in the Copiapó area are hosted in Lower Tertiary (Eocene) felsic rocks (Sato, 1984; Rodríguez X., pers. comm., XXX).

The host rock volcanics are generally characterized by monoclinal sheet-like extrusions with basaltic to rhyodacitic compositions. Typical bimodal volcanic rock suites of basalt and rhyodacite association are observed in the Santiago area (e.g. Vergara *et al.*, 1995; Boric *et al.*, 2002; Wilson *et al.*, 2003a, b). This is regarded as the characteristic of volcanism under extensional tectonic stress, as suggested for the Japanese Kuroko districts (Urabe, 1987). The host volcanic rocks show various textures, such as porphyritic (ocoitic), amygdaloidal and aphanitic, and consist of calc-alkaline to subordinate tholeiitic and alkaline members (Levi *et al.*, 1988; Klohn *et al.*, 1990; Morata & Aguirre, 2003; Kramer *et al.*, 2005; Lucassen *et al.*, 2006). All of the volcano-sedimentary sequences hosting manto-type copper deposits have

Table 1 Synopsis of geological characteristics of principal Chilean manto-type deposits

Area	Host rock lithology	Principal deposit	Copper sulfides	Age (Ma)	Main references
Arica–Iquique	Jurassic (Aalenian – Oxfordian) Camaraca and Oficina Viz F., andesitic rocks with subordinate marine sediments	Casa Grande-Argolla	Cc, Cv> Bn > Cp	—	MINDES (1989); Kramer *et al.* (2005); Oliveros *et al.* (2006)
Tocopilla–Taltal	Jurassic (Pliensbachian – Aaleian) La Negra F., andesitic rocks with subordinate marine sediments	Michilla (Lince–Estefanía, Buena Vista)	Cc, Bn, Cv > Cp	*ca* 160 (Re-Os)	Venegas *et al.* (1991); Kojima *et al.* (2003); Tristá-Aguilera *et al.* (2006)
Copiapó	Lower Cretaceous (Berremian Aptian) Pabellón F., andesitic rocks with marine carbonates	Ocoita-Pabellón Metallotect	Cp, Bn > Cc, Cv, Tr	—	Marschik and Fontboté (2001); Cisterna and Hermosilla (2006)
La Serena	Lower Cretaceous (Hauterivian – Albian) Arqueros and Quebrada Marquesa F., andesitic rocks with limestone	Talcuna	Cp, Bn > Cc, Cv, Tr	—	Boric (1985); Camus (1990); Oyarzun *et al.* (1998)
Santiago	Lower Cretaceous (Berriasian – Barremian) Lo Prado and Veta Negra F., bimodal volcanic rocks with marine sediments	El Soldado	Bn, Cc, Cp	103 ± 3 (Ar-Ar)	Boric *et al.* (2002); Wilson *et al.* (2003a, b); Carrillo-Rosúa *et al.* (2006)

Time scale after Gradstein *et al.* (2004).
Bn, bornite; Cc, chalcocite-digenite; Cp, chalcopyrite; Cv, covellite (secondary); F, Formation; Tr, tetrahedrite-tennantite.

considerable thickness over at least 2 km, and thus underwent prograde zeolite to lower greenschist facies regional (or burial) metamorphism (Levi, 1969, 1970; Palacios, 1977; Wilson *et al.*, 2003b; Shiba *et al.*, 2006).

Voluminous plutonic complexes emplaced during the Jurassic–Early Cretaceous are normally observed in the mining districts of all the areas, and have intimate spatial relations with the orebodies in the northern area deposits. In contrast, the plutonic intrusions are located on sectors fairly separated from the orebodies in some central area mining districts, such as Talcuna (Oyarzun *et al.*, 1998) and El Soldado (Boric *et al.*, 2002). These complexes occur as basic to felsic stocks and dikes of calc-alkaline members, and are composed predominantly of gabbro, diorite, monzonite, granodiorite and quartz monzonite with the I-type magnetite-series characteristics (Ishihara *et al.*, 1984; Marschik *et al.*, 2003).

The northern area deposits in the Coastal Cordillera are situated nearby the main branches of the N–S-trending Atacama fault zone, which extends >1000 km along the Chilean coastal range between Iquique and La Serena. This zone is characterized by the sinistral strike–slip faults formed during transtensional oblique subduction in the Jurassic–Early Cretaceous (e.g. Scheuber & Andriessen, 1990), and typical strike–slip duplex structures of the main fault zone prevail in the Iquique to Taltal districts (Cembrano *et al.*, 2005). A transtensional sinistral strike–slip brittle shear system is also identified in the Santiago area (Boric *et al.*, 2002).

3. Characteristics of alteration and primary mineralization

Normally, host rocks in the vicinity of orebodies have experienced hydrothermal alteration genetically linked to primary copper mineralization. This event is commonly characterized by extensive sodic alteration (albitization) and consecutive calcic alteration of epidote, calcite, chlorite, sericite, Ca-amphibole (actinolite) and quartz (Elgueta *et al.*, 1990; Klohn *et al.*, 1990; Wolf *et al.*, 1990; Oyarzun *et al.*, 1998; Kojima *et al.*, 2003; Cisternas & Hermosilla, 2006). Moreover, pervasive potassic alteration as observed in the iron oxide–copper–gold (IOCG) deposits occurs in the Mantos Blancos deposit. This alteration is dominated by biotite and/or K-feldspar with minor tourmaline, and is regarded as an earlier event prior to the propylitic alteration at the Mantos Blancos deposit (Ramírez *et al.*, 2006).

Primary copper mineralization usually occurs as dissemination, amygdule-filling, stockwork and thin veinlet in host rocks (Sato, 1984; Kojima *et al.*, 2003). Sato (1984) classified the North Chilean manto-type deposits into the following three types according to their modes of occurrence: (1) stratabound tabular type (e.g. Talcuna, Cerro Negro); (2) stacked tabular type (e.g. Buena Esperanza, Lince–Estefanía); and (3) pseudostratiform type (e.g. Mantos Blancos, El Soldado, Lo Aguirre). The type 1 deposits have many fine laminae in a singular stratigraphic horizon of host rocks, while in the type 2 deposits many stratiform orebodies occur selectively in porous units, such as amygdaloidal flows. In several type 2 deposits (e.g. Buena Esperanza, Lince–Estefanía), breccia pipe develops surrounding unmineralized gabbroic to dioritic dike, and also the breccia zone is partially mineralized. The type 3 deposits are composed of irregularly-shaped ore zones, structurally controlled by localization of lateral faults and associated feeder dikes (e.g. Boric *et al.*, 2002). Thus, the types 2 and 3 deposits exhibit epigenetic modes of occurrence. In the case of the type 1 deposits, the mineralized zones are intimately associated with other modes of orebodies, such as veinlets and breccia fillings as the mineralization channel ways, and generally occur in permeable horizons favorable to mineralization (Camus, 1990; Elgueta *et al.*, 1990). These features suggest that the type 1 deposits could also be epigenetic.

In the copper mineral species occurring in the deposits, certain differences are recognized in the respective areas (Table 1): chalcocite (-digenite)–bornite association is predominant in the northern areas, but chalcopyrite occurs as a principal mineral in the central areas. In addition to the aforementioned minerals, lesser amounts of pyrite, native copper, native silver, tetrahedrite–tennantite, galena, sphalerite, magnetite and hematite are sporadically observed as the primary minerals (Camus, 1990; Wolf *et al.*, 1990; Oyarzun *et al.*, 1998; Kojima *et al.*, 2003; Ramírez *et al.*, 2006; Tristá-Aguilera, 2007), and arsenopyrite, marcasite, enargite, safflorite, carrollite and stromeyerite are rarely reported in several central area deposits (Carrillo-Rosúa *et al.*, 2006; Rodríguez, pers. comm.). In the El Soldado deposit and Ocoita-Pabellón Metallotect district (Copiapó area), such organic matter as solid bitumen and pyrobitumen are found in close relation with primary ore minerals (Zentilli *et al.*, 1997; Wilson & Zentilli, 1999; Wilson *et al.*, 2003b; Cisternas & Hermosilla, 2006).

Fluid inclusion studies were carried out on quartz and calcite associated with primary copper minerals, and significant data on formation conditions of the primary mineralization have been given (Table 2). Primary fluid inclusions observed consist generally of CO_2-free liquid + vapor and liquid + vapor + salt (NaCl) inclusions, and vapor-dominant gaseous inclusions occasionally coexist with them (e.g. Nisterenko *et al.*, 1973; Kojima *et al.*, 2003; Ramírez *et al.*, 2006). The coexistence of liquid (or polyphase) and gaseous inclusions is evidence for fluid boiling, and suggests that the hypogene mineralization occurred under relatively low-pressure conditions. This effect could explain the marked difference in salinity shown in Table 2. In the deposits of the Ocoita-Pabellón Metallotect district, crude oil is reported in liquid-rich fluid inclusions (Cisternas & Hermosilla, 2006). Recently, Tristá-Aguilera (2007) applied the chlorite geothermometer of Cathelineau (1988) to the primary mineralization of the Lince–Estefanía deposit (Michilla district), and gave mineralization temperatures ranging 230–299°C. This is consistent with the result of the fluid inclusion study (Table 2). Thus, hydrothermal brines with temperatures mostly in the range 150–360°C common to most hydrothermal copper deposits are regarded to have been responsible for the manto-type copper mineralization.

4. Constraints from isotope geochemistry

Current progresses of isotope studies could contribute to the manto-type deposit metallogeny, but it appears that those have not yet led to a uniform conclusion on the source of ore-forming elements and hydrothermal water. In this chapter we review recent isotope studies on the Chilean manto-type deposits.

4.1 Heavy metallic element isotopes

$^{207}Pb/^{204}Pb - ^{206}Pb/^{204}Pb$ isotopic characteristics of primary copper minerals from representative deposits, associated igneous rocks and contemporaneous sedimentary rocks for the northern (Jurassic) and central (Lower Cretaceous) areas are depicted, respectively, in Figure 2. The Pb isotopic ratios of the central area deposits hosted in volcanic-dominant piles (El Soldado, Lo Aguirre) and in volcano-sedimentary piles (Talcuna, Cerro Negro) are markedly homogeneous, and are close to the isotope ranges of the related igneous rocks (Tosdal & Munizaga, 2003). The igneous rocks (Early Cretaceous volcanic and plutonic rocks) are

Table 2 Summary of primary fluid inclusion data for principal Chilean manto-type deposits

Deposit	Mineral used	Inclusion type	T_H range (°C)	Salinity†	References
Buena Esperanza	Calcite, Quartz	L + V, V + L	64–235	—	Nisterenko *et al.* (1973)
	Quartz	L + V + S (NaCl)	440–500	52–59	Palacios (1990)
Mantos de La Luna	Calcite	L + V, V + L, L + V + S (NaCl)	163–350	25–34	Kojima *et al.* (2003)
Michilla					
Lince–Estefanía	Quartz, Calcite	L + V, V + L	151–509	3.7–20.5	Kojima *et al.* (2003)
Buena Vista	Quartz	L + V	214–360	16–21	Kojima *et al.* (2003)
Mantos Blancos	Quartz	L + V, V + L, L + V + S (NaCl)	187–601	2.5–62	Ramírez *et al.* (2006)
Ocoita-Pabellón	Calcite	L + V, V + L, L + V + oil	116–404	3.5–25.3	Cisternas and Hermosilla (2006)
Metalotect					
Talcuna	Calcite	L + V	120–205	11–19	Oyarzun *et al.* (1998)
El Soldado	Quartz, Calcite	L + V, L + V + S	93–303	3–31	Holmgren (1987); Klohn *et al.* (1990); Boric *et al.* (2002)
El Salado	Quartz	L + V, V + L, L + V + S (NaCl)	249–430	High	Nisterenko *et al.* (1973)
Lo Aguirre	Quartz, Calcite	L + V, L + V + S (NaCl)	140–240	1.5–34	Saric *et al.* (2003)

†Equivalent to wt. % NaCl.L, liquid; S, solid; T_H, homogenization temperature; V, vapor.

also isotopically homogeneous, and have slightly lower $^{207}Pb/^{204}Pb$ values than the ore leads. These features suggest that the central area ore lead is mostly of igneous origin with a slight contribution of Cretaceous sediment-derived lead (Tosdal & Munizaga, 2003).

By contrast, the Pb isotope ratios of the Tocopilla–Taltal area deposits are fairly scattered, and show significantly more radiogenic compositions than those of the Lower Cretaceous areas. This phenomenon is interpreted as due to contamination of Jurassic sediment-derived lead, which has a wide range of uranogenic compositions (Fig. 2). The presence of pre-Mesozoic (Paleozoic) basement (Arequipa-Antofalla terrane), which is composed predominantly of gneiss and granitoids, is seen in the northern areas (e.g. Bahlburg & Hervé, 1997; Lucassen *et al.*, 1999). Ore lead contamination with the Paleozoic basement should be also assumed, but the Pb isotope range of the basement rocks is separated from that of the ore lead values (Fig. 2). In consequence, the Paleozoic basement rocks are regarded to be unlikely as an origin of the ore lead. The Tocopilla–Taltal area ore leads fall close to the average crustal growth curve (Stacey & Kramers, 1975), suggesting that the ore leads could be identified as crustal lead in their origin. By contrast, the central area ore leads have slightly lower ranges in both $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios than those of the Tocopilla–Taltal area deposits. This suggests less assimilation of crustal lead, and may reflect the minor thickness of the central area continental crust (Macfarlane *et al.*, 1990).

A similar feature has been also detected in Os isotope as a good proxy to estimate origin of ore-forming chalcophile metals (Ruiz *et al.*, 1997; Tristá-Aguilera *et al.*, 2006). Table 3 lists the initial $^{187}Os/^{188}Os$ ratios of primary copper sulfides from the Lince–Estefanía (1.06) and El Soldado (3.94977), which are much higher than those of the continental mantle (0.128 ± 0.006; Brandon *et al.*, 1996). These radiogenic compositions indicate that the crustal source Os was responsible for the manto-type ore mineralization. Particularly, the El Soldado ore lead has an extremely high $^{187}Os/^{188}Os$ ratio, which could be accounted for by contribution of high Re/Os crustal reservoir, such as black shale (Ruiz *et al.*, 1997). This interpretation is consistent with the aforementioned geologic features of the area, and also the sulfur and carbon isotope characteristics mentioned in the following section.

4.2 Light element isotopes

In contrast to the Pb isotopes, sulfur isotope compositions of primary copper sulfides from the northern areas are fairly homogeneous, displaying mostly slightly negative ranges (Table 4). These uniform isotopic compositions strongly suggest a singular igneous source of ore-forming sulfur. In contrast, the copper sulfides from several deposits of the central areas (Ocoita-Pabellón Metallotect, Talcuna, Cerro Negro, El Soldado) have an extremely wide range of isotopic compositions from negative values (minimum $\delta^{34}S$ = −44.7‰) to positive values (maximum $\delta^{34}S$ = +19.0‰).

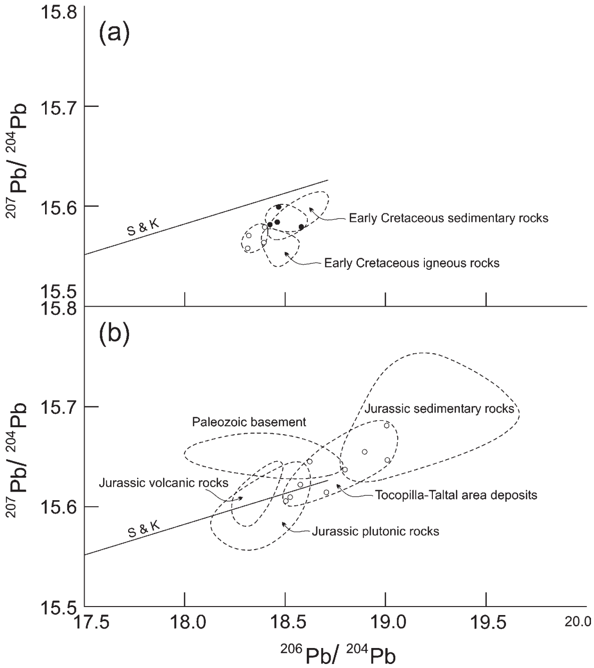

Fig. 2 Lead isotope diagrams showing isotopic ranges of ore lead and associated rocks in (a) Lower Cretaceous and (b) Jurassic areas. Data from Vivallo and Henríquez (1998), Lucassen *et al.* (1999, 2006), Tosdal and Munizaga (2003), Thompson *et al.* (2004) and Kramer *et al.* (2005). Sample localities of the Jurassic (Tocopilla–Taltal) area deposits are not shown clearly in Vivallo and Henríquez (1998). Average crustal growth curve (S & K) is after Stacey and Kramers (1975). (●) Volcanic-dominant pile-hosted deposits: Lo Aguirre–El Soldado; (○) volcano-sedimentary pile-hosted deposits: Talcuna–Cerro Negro.

This wide range of δ^{34}S is generally considered to be due to a contribution of evolved biogenic sulfur mediated kinetically by bacterial sulfate reduction (Wilson *et al.*, 2003b); indeed, the central area districts are geologically characterized by evaporate-rich sedimentary basins (Oyarzun *et al.*, 1998).

Principal carbon and oxygen isotope data of hydrothermal calcite associated with primary copper minerals are summarized in Figure 3, together with the composition ranges of igneous carbonates, marine carbonates and organically derived carbon. Although simple comparison is not adequate because of the lack of data for a few deposits, a marked difference in δ^{13}C range is observed: the calcite carbons of the northern area deposits generally display less negative δ^{13}C, that is, −6.9 to −0.8‰, but those of the central area deposits are widely distributed in a noticeably negative value range, particularly in the El Soldado (δ^{13}C = −20.2 to −4.2‰). In the case of the El Soldado deposit, most calcite carbons fall in the organic carbon range (Fig. 3). This suggests a major contribution of biogenic carbon, such as pyrobitumen-associated oxidized matter (Wilson *et al.*, 2003b).

Kojima *et al.* (2003) have suggested, based on isotopic fractionation of carbon at temperatures inferred from fluid inclusion data, that the Lince–Estefanía calcite carbon is derived from either igneous carbon or sedimentary carbonate intercalated in the host rocks (La Negra Formation). In contrast, the δ^{18}O of calcite from the northern area deposits, particularly from the Mantos Blancos, have wide ranges extending toward ^{18}O-rich compositions. It is not clear whether the phenomenon depends on thermal effect on isotopic fractionation between calcite and mineralizing fluid or incorporation of sediment-derived ^{18}O-rich components, because formation temperatures for the corresponding calcite have not been obtained. Figure 3 shows that most δ^{13}C and δ^{18}O of the northern area calcites analyzed are distributed between those of igneous carbonates and marine carbonates. This relation leads us to infer that the carbonate components would be from both igneous and sedimentary sources.

Furthermore, some ^{87}Sr/^{86}Sr initial ratios of hydrothermal calcites are reported for El Soldado deposit (Wilson *et al.*, 2003b) and three Tocopilla–Taltal area deposits (Vivallo & Henríquez, 1998). Their composition ranges are shown in Figure 4, together with those of the associated igneous rocks and contemporaneous seawater. The ^{87}Sr/^{86}Sr ratios of the El Soldado and Mantos de la Luna are close to those of the igneous rocks, and so their calcite-forming fluids are inferred to have been equilibrated with the associated volcanic rocks. By contrast, the Mantos Blancos and Santo Domingo calcites display much higher ^{87}Sr/^{86}Sr ratios than those of the associated igneous rocks. This is explained by a certain contribution of surface-derived Sr as included in the

Table 3 Os isotopic compositions of primary copper sulfide minerals from Chilean manto-type deposits

Deposit	Mineral	Initial ^{187}Os/^{188}Os	References
Lince–Estefanía (Michilla)	Chalcocite (+bornite)	1.06 ± 0.09	Tristá-Aguilera *et al.* (2006)
El Soldado	Chalcopyrite	3.94877	Ruiz *et al.* (1997)
Continental mantle		0.122–0.134	Brandon *et al.* (1996)

Table 4 Summary of sulfur isotope compositions for primary copper sulfide minerals from principal Chilean manto-type deposits

Deposit	Copper phase	$\delta^{34}S$ (‰) range (no. analyses)	References
Buena Esperanza	composite	−0.3 (1)	Sasaki *et al.* (1984)
Mantos de La Luna	cc-dg	−2.1 to −1.6 (2)	Present study
Mantos del Pacífico	bn	−6.6 to −6.2 (2)	Vivallo and Henríquez (1998)
Michilla			
Lince–Estefanía	cc	−5.7 to −3.0 (3)	Vivallo and Henríquez (1998)
	cc-dg (-bn)	−5.2 to +2.1 (12)	Sasaki *et al.* (1984); Munizaga and Zentilli (1994); Vivallo and Henríquez (1998); Tristá-Aguilera (2007)
	Cp	0.0 (1)	Sasaki *et al.* (1984); Munizaga and Zentilli (1994); Vivallo and Henríquez (1998); Tristá-Aguilera (2007)
Buena Vista	cc-dg	−3.8 to −3.1(3)	Present study
Mantos Blancos	cc-dg	−3.2 to −0.1 (7)	Sasaki *et al.* (1984); Munizaga and Zentilli (1994); Ramírez *et al.* (2006)
	cp-py	−4.5 to +1.2 (6)	Sasaki *et al.* (1984); Ramírez *et al.* (2006)
Santo Domingo	bn	−2.3 (1)	Vivallo and Henríquez (1998)
Ocoita-Pabellón	bn-cp-tr	−44.7 to −25.4 (6)	Cisternas and Hermosilla (2006)
Metalotect	cc-cv	−21.9 to −17.9 (2)	
Talcuna	cc-bn-cp	−38.3 to −16.0	Puig and Spiro (1988); Carrillo-Rosúa *et al.* (2006)
Cerro Negro	bn	−21.2 to −15.7 (3)	Munizaga *et al.* (1994)
	cp	−21.2 to −15.6 (3)	Munizaga *et al.* (1994)
El Soldado	cc	−12.7 to −4.6 (2)	Villalobos (1995); Wilson *et al.* (2003b)
	cc-bn	−2.2 to +15.2 (6)	Villalobos (1995); Wilson *et al.* (2003b)
	bn	−6.9 to +10.5 (10)	Klohn *et al.* (1990); Wilson *et al.* (2003b)
	bn-cp	−4.1 to +19.0 (5)	Klohn *et al.* (1990); Wilson *et al.* (2003b)
	cp	−6.8 to +7.7 (13)	Klohn *et al.* (1990); Villalobos (1995); Wilson *et al.* (2003b)
	cp-py	−5.2 to +12.6 (6)	Klohn *et al.* (1990); Wilson *et al.* (2003b)
El Salado	bn-cc	−1.3 (1)	Sasaki *et al.* (1984)
Lo Aguirre	bn-cc-cp-py	−3.6 to +1.4 (4)	Puig and Spiro (1988); Saric *et al.* (2003)
Melipilla	cc-bn-cp	−36.9 to −16.0	Carrillo-Rosúa *et al.* (2006)

bn, bornite; cc, chalcocite; cp, chalcopyrite; cv, covellite; dg, digenite; py, pyrite; tr, tetrahedrite.

contemporaneous seawater ($^{87}Sr/^{86}Sr$ = 0.7067–0.7076; Veizer *et al.*, 1999) and the aforementioned sedimentary carbonate ($^{87}Sr/^{86}Sr$ = 0.7067; Venegas *et al.*, 1991).

Hydrogen and oxygen isotope data are indispensable to estimate origin of hydrothermal water responsible for the primary copper mineralizations. Available data on the isotopes, however, have not yet been obtained, and thus this is an important subject that should be solved in the future.

5. Discussion

Historically, syngenetic versus epigenetic theories have been debated (e.g. Ruiz *et al.*, 1965, 1971; Sato, 1984; Boric, 1985; Camus, 1990; Vivallo & Henríquez, 1998; Kojima *et al.*, 2003), and several genetic models have been proposed for the Chilean manto-type copper deposits. Those are summarized in the following three theories: (i) syngenetically formed volcanogenic deposits (Ruiz *et al.*, 1965, 1971); (ii) epigenetic deposits formed by magmatic emanation of associated plutonic intrusions (e.g. Palacios, 1986, 1990; Vivallo & Henríquez, 1998); and (iii) epigenetic deposits formed by fluid–rock interaction involving Cu-bearing host rocks (Losert, 1973, 1974; Sato, 1984; Tosdal & Munizaga, 2003).

Congruent sets of all of the isotope data have been obtained for only several deposits, but those could provide key information for the formation mechanism of primary copper ores.

5.1 Volcanic-derived syngenetic theory

Based on the presence of discrete copper sulfide grains with no gangue minerals in the groundmass of andesitic host rocks, Ruiz *et al.* (1965, 1971) insisted on the

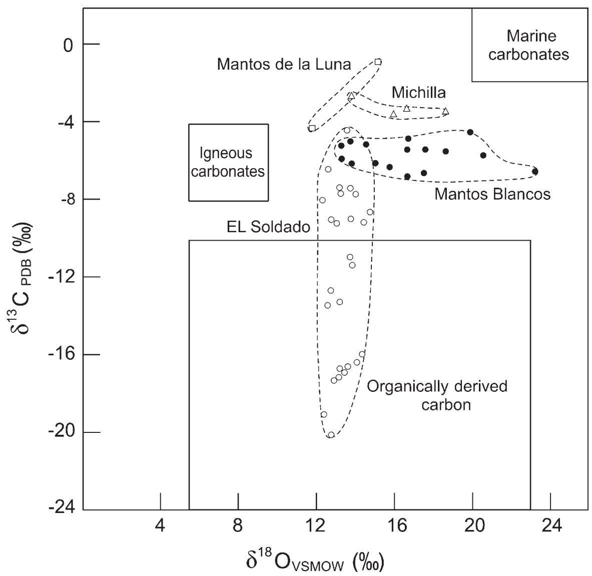

Fig. 3 Carbon and oxygen isotope compositions of hydrothermal calcites from principal Chilean manto-type copper deposits. Data from Vivallo and Henríquez (1998), Wilson *et al.* (2003b), Kojima *et al.* (2003) and Ramírez *et al.* (2006). Fields for normal igneous carbon, marine carbonates and organically derived carbon are from Valley (1986) and Longstaffe (1989).

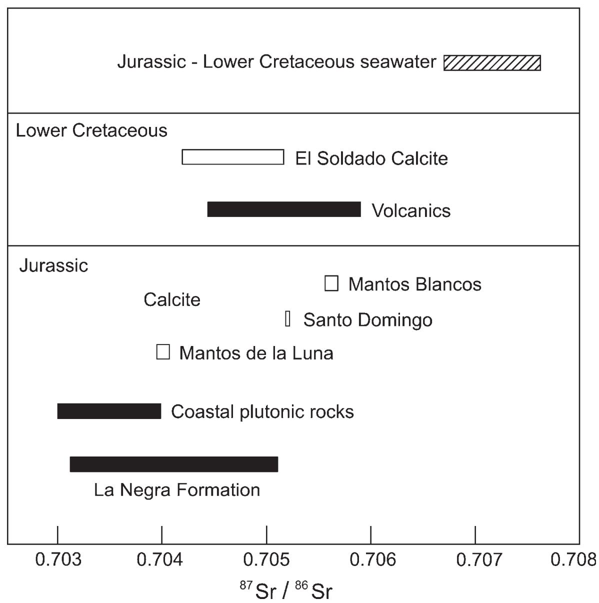

Fig. 4 $^{87}Sr/^{86}Sr$ ratios of hydrothermal calcites from the El Soldado deposit and three Tocopilla–Taltal area deposits, compared with those of associated igneous rocks and contemporaneous seawater. The $^{87}Sr/^{86}Sr$ ratio of the La Negra Formation limestone (Viruca at the southern Michilla district; Venegas *et al.*, 1991) is included in the seawater range (Koepnick *et al.*, 1985; Veizer *et al.*, 1999). Other data from McNutt *et al.* (1975), Rogers and Hawkesworth (1989), Tassinari *et al.* (1993), Pichowiak (1994), Vivallo and Henríquez (1998), Lucassen *et al.* (2002, 2006), Wilson *et al.* (2003b) and Tristá-Aguilera (2007).

syngenetic–magmatic theory for all the types of manto-type deposits. For the disseminated copper mineralization in sediment-rich horizons, they suggested contemporaneous cupriferous volcanic exhalations. The geochronologic data in Table 1, however, indicate that the ages of primary mineralization are generally younger that those of the host rocks, and the primary fluid inclusion data clearly indicate hydrothermal temperatures. In consequence, this “syngenetic” theory (theory 1) is discarded.

5.2 Pluton-derived epigenetic theory

The epigenetic formation processes of theories 2 and 3, as illustrated in Figure 5, are detailed.

Magmatic source (theory 2) or leaching of igneous components (theory 3) is supported by the uniform Pb and S isotope compositions of primary copper minerals. As noted earlier, the gabbroic to dioritic dike intrusions are closely associated with primary mineralized zones in the stacked tabular type of deposits, such as the Buena Esperanza and Lince–Estefanía in the Tocopilla–Taltal area. Moreover, it has been known that a zonal distribution of primary copper minerals occurs in spatial concordance with the gabbro-dioritic intrusion in the Buena Esperanza and Santo Domingo deposits (Definis, 1985; Espinoza *et al.*, 1996). These features seem to support theory 2. A clear spatial relationship, however, between ore zone and intrusion is not confirmed in the central area deposits (e.g. Camus, 1990). Furthermore, all of the isotope data presented in the previous chapter strongly suggest contribution of crustal components including sedimentary rock units. Thus, it is not favorable to regard the intrusion magma as the main source of ore-forming components, although local incorporation of magmatic fluid and thermal effect of the intrusion should be taken into account (Kojima *et al.*, 2003).

5.3 Host rock-derived epigenetic theory

Theory 3, which estimates the host rocks as the source of the ore-forming components, appears to be most probable at present. The reason for this lies in the appreciable influx of sedimentary rock components, as inferred from Pb, Os, S and C isotope data for the principal deposits and the Sr isotope data for a few Tocopilla–Taltal area deposits. Furthermore, several geochemical studies on the host volcanics also support the host-rock origin theory; for example Zentilli (1974) noted that Chilean

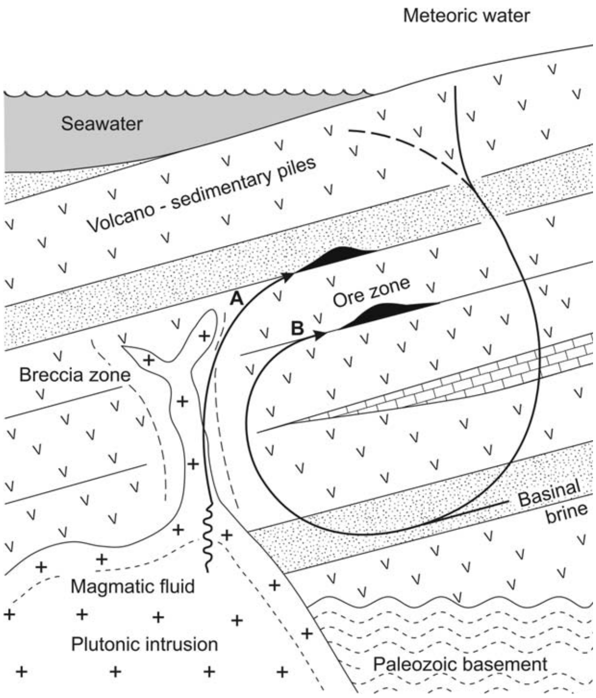

Fig. 5 Schematic illustration showing alternative genetic models for Chilean manto-type copper deposits. (A,B) Flow paths of magmatic emanation and surface water leaching, respectively. Host rock is volcano-sedimentary piles composed of andesite-dominant volcanic rocks, tuffaceous sandstone and limestone. Local faults are not shown.

Jurassic andesites had high Cu contents (90–375 ppm) compared with Cenozoic andesites (10–32 ppm), and Campano and Guerra (1975) indicated that Cu amounts in the La Negra Formation basaltic rocks decreased significantly after hydrothermal epidotization. These results suggest that high amounts of Cu were initially contained in the Mesozoic host rocks, and that those were leached during the hydrothermal alteration.

The following two distinct ideas are presented regarding the source of hydrothermal water responsible for the primary copper mineralization. First, metamorphic water generated in the low-grade regional (burial) metamorphism was assumed as the main source (Losert, 1973, 1974; Sato, 1984). In this condition the thermal effect of the associated intrusions is not particularly required to be taken into account. A second possible source is surface-derived fluids such as meteoric water and seawater including deeper basinal brine (Kojima *et al.*, 2003; Tosdal & Munizaga, 2003). This case requires a heat source such as an igneous body to drive thermal convection of the surface-derived waters.

Shiba *et al.* (2006) carried out detailed phase analyses of metamorphic minerals for the La Negra Formation host rocks distributed in the coastal range of the Tocopilla to Antofagasta province, and estimated *P-T* conditions of 200–310°C and approximately 1.75 kb for the burial metamorphism. The temperature range is nearly identical to that inferred from the fluid inclusion studies. The pressure of approximately 1.75 kb, however, is too high to cause the fluid boiling, which is observed in the fluid inclusions studied (Table 2). It is still unknown whether or not fluid boiling is the principal mechanism of precipitation of primary copper ores, but the aforementioned discrepancy shows that the metamorphic water related to the burial metamorphism could not be the direct mineralizing fluid responsible for the primary copper ore formation.

Alternatively, it is more likely that the mineralizing fluid was essentially generated in the process of surface-derived water circulation in the volcano-sedimentary sequence induced by a deep-seated intrusion. Particularly, basinal brine is regarded as the important fluid source, judging from the high salinities of observed primary fluid inclusions (Oyarzun *et al.*, 1998; Kojima *et al.*, 2003; Wilson *et al.*, 2003a). Wilson *et al.* (2003a) detected high levels of atmospheric Ar in hydrothermally precipitated K-feldspar samples associated with primary copper sulfides. This indicates that connate meteoric water was incorporated into the basinal brine. Kojima *et al.* (2003) suggested mixing of high-temperature meteoric water with cooler basinal brines, based on the negative correlation in the temperature–salinity relation of fluid inclusions from the Mantos de la Luna, Lince–Estefanía and Buena Vista deposits.

6. Summary and conclusions

This study summarizes the general geology, mineralogy, fluid inclusion data and stable isotope characteristics of the Chilean manto-type (volcanic redbed) copper deposits, and suggests a possible mechanism constrained particularly from the isotope data.

Not only the modes of occurrence but also the geochronologic and fluid inclusion data indicate that the manto-type deposits are epigenetic hydrothermal deposits occurring mostly in the Early Upper Jurassic (northern areas) to Late Lower Cretaceous (central areas). The uniform Pb and S isotope compositions of primary copper minerals imply signature of magmatic source or leaching of igneous components. All the Pb isotope data, however, lie on a range between the associated igneous and sedimentary host rocks, suggesting that ore-forming metals were derived from the volcano-sedimentary host rocks. The influx of sedimentary rock components is strongly suggested from the extremely negative isotope ratios of primary sulfide sulfur and hydrothermal calcite carbon, given for samples from several central area deposits. In addition, the high $^{87}Sr/^{86}Sr$ initial ratios of hydrothermal calcite from a few Tocopilla–Taltal area deposits suggest influx of seawater or marine carbonates. Thus, hydrothermal interaction of such surface-derived waters as meteoric water and basinal brine with the volcano-sedimentary host rocks appears to be a highly probable genetic mechanism for the normal manto-type deposits. A regional heat source is needed to circulate the surface-derived water within the host rocks, and a deep-seated plutonic complex could be regarded to have played a significant role as the probable heat source. Thus, local geology characteristics, including host rock lithology and intrusion emplacement, should be well clarified to specifically model the manto-type copper deposits in the respective areas.

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