The Distribution and Timing of Molybdenite Mineralization at the El Teniente Cu-Mo Porphyry Deposit, Chile

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Abstract

The El Teniente Cu-Mo porphyry deposit, Chile, is one of the world’s largest and most complex porphyry ore systems, containing an estimated premining resource of approximately 95 Mt Cu and 2.5 Mt Mo. Although Cu mineralization at the deposit is quite well studied, little work has focused specifically on the distribution and timing of Mo mineralization. Combined grade, vein, and breccia distribution analysis reveals that deposit-wide Mo grades of 0.01 to 0.06 wt % are strongly controlled by the abundance of main mineralization (type 6a) quartz ± molybdenite veins. These show a clear spatial relationship with several felsic-intermediate intrusions and appear to develop outward and upward into Cu-rich (type 6b–7b) quartz-chalcopyrite veins and (type 8) chalcopyrite-anhydrite ± bornite veins with sericitic alteration halos. High-precision Re-Os molybdenite dating reveals that these linked vein types did not develop in a single, deposit-wide evolution, but are diachronous, related to distinct episodes of hydrothermal activity associated with the emplacement of diorite finger porphyries and the composite Teniente Dacite Porphyry. These units acted as effective, short-lived (<100,000 years) conduits for pulses of Mo- and Cu-bearing hydrothermal fluids between 6.3 and 4.6 Ma. The rapid thermal contraction of each system during mineralization led to extensive overprinting of Mo-rich veins by their lower-temperature, Cu-rich equivalents. Separate pulses in magmatic-hydrothermal activity are separated by distinct gaps of up to 300,000 years, during which Mo-mineralizing activity appears to have gone into quiescence.

Mo grades exceeding 0.06 wt % correspond to the presence of molybdenite-bearing, late mineralization-stage, tourmaline-cemented (type 9), and anhydrite-carbonate ± gypsum (type 10) veins and breccias. These are abundant at shallow mine levels and show a close spatial relationship with a series of concentric faults associated with the Braden Breccia Pipe. Mineralization in this paragenetic stage is relatively short-lived and occurs in all parts of the deposit between 4.80 and 4.58 Ma. The generally Cu poor nature of the late mineralization stage is attributed to the prior preferential extraction of Cu from the underlying magma chamber in earlier mineralizing events. This led to the late exsolution of oxidized, Mo-rich fluids that may have undergone further enrichment by remobilizing Mo from main mineralization-type veins associated with the Teniente Dacite Porphyry. The formation of the Braden Breccia Pipe is likely to have occurred in a single cataclysmic event at approximately 4.58 Ma, which cut the Mo-rich tourmaline breccias and created a distinct Mo-rich grade halo at shallow mine levels. With the exception of minor mineralization associated with small dacitic dikes at approximately 4.42 Ma, the Braden event marked the termination of Mo deposition.

Introduction

The El Teniente Cu-Mo porphyry deposit, Chile (34°05′S, 70°21′W), is located approximately 70 km southeast of Santiago (Fig. 1) on the western margin of the Andean Cordillera and within the confines of the central Chilean porphyry Cu belt. This supergiant porphyry is the world’s largest underground Cu mine, hosting a premining resource of approximately 95 Mt of fine Cu (Camus, 2002; Stern et al., 2010). Molybdenum, present in the form of molybdenite, is obtained purely as a by-product of Cu mining with typical ore grades of <0.03 wt %. However, the great size of El Teniente makes it the world’s largest known resource of Mo (Sillitoe, 2010) with a current and mined resource total of approximately 2.5 Mt (Camus, 2002). Despite this, relatively little attention has focused on the distribution and timing of Mo mineralization. Such information is important for developing the Mo resources at the mine and can enhance our understanding of the magmatic and hydrothermal fluids responsible for Mo transportation and mineralization in porphyry systems.

Geologic relationships (e.g., Cannell et al., 2005; Vry et al., 2010), paleomagnetism (Astudillo et al., 2010), and Re-Os dating of molybdenite (Cannell, 2004; Maksaev et al., 2004) indicate that mineralization at El Teniente resulted from multiple brecciation-veining events associated with the emplacement of a number of felsic-intermediate intrusions. Molybdenite is interpreted to have been precipitated in every alteration and mineralization stage at the deposit, but in highly variable amounts (e.g., Hernández et al., 1980; Cuadra, 1986). Locally, there is also evidence for overprinting of early Mo-bearing vein stages by later molybdenite (Cannell et al., 2005; Vry et al., 2010). This apparent multiphase evolution means that there is still uncertainty regarding the most important intrusions, breccias, and veins with respect to Mo introduction.

A recent study at El Teniente highlighted the distinct decoupling in the spatial distribution of Mo and Cu (Vry et al., 2010). Similar decoupled zonation patterns have been recognized at a number of other porphyry deposits (e.g., El...
Salvador, Chile; Gustafson and Hunt, 1975; Bajo de la Alumbra, Argentina: Ulrich and Heinrich, 2001; Butte, Montana: Rusk et al., 2008; Bingham Canyon, Utah: Landtwing et al., 2010; Redmond and Einaudi, 2010; Seo et al., 2012). At Bingham Canyon this was attributed to reduction and an increase in acidity in the evolving fluid source region (Seo et al., 2012). This led to the initial exsolution of oxidized fluids, which favored the early transport and deposition of Cu and retarded Mo deposition. Subsequent exsolution of more reduced and acidic fluids then favored molybdenite saturation, creating an Mo-rich vein overprint. At El Teniente, molybdenite-rich veins are commonly overprinted by chalcopyrite, suggesting different controls on decoupling (Vry et al., 2010). In order to identify these controls, better constraints on the distribution and timing of molybdenite mineralization relative to Cu sulfide deposition are required. These include accurate identification of the veins and breccias that are the most important hosts for Cu and Mo sulfides and their timing relationships in different parts of the deposit.

By combining grade distribution data with detailed drill core analysis, this study aims to provide quantitative constraints on the distribution and abundances of different vein and breccia types and determine their relationships with Mo and Cu mineralization. In addition, Re-Os molybdenite geochronology was used in an attempt to provide better constraints on the timing of mineralization across the deposit. This technique is ideal because the ore mineral of interest is dated directly and the geochronometer displays closed behavior during
postmineralization hydrothermal alteration—an important factor in multistage mineralizing systems such as El Teniente (e.g., Stein et al., 1998; Selby and Creaser, 2001; Stein and Bingen, 2002; Bingen and Stein, 2003; Ootes et al., 2007; Bingen et al., 2008; Lawley and Selby, 2012). Previously, 18 molybdenite samples were dated at El Teniente using this technique (Cannell, 2004; Maksaev et al., 2004). These studies provided a general timescale for Mo mineralization but had several limitations:

1. They only provided age determinations for molybdenite in a few vein and breccia types and excluded some Mo-rich stages, including veins and breccias related to the late mineralization stage;
2. They used samples that were predominantly obtained from shallow mine levels in Cu-rich parts of the deposit;
3. They did not date molybdenite associated with a number of economically important intrusions and fault zones;
4. They did not date different vein generations in a particular part of the deposit and therefore provided little information regarding the potential longevity of mineralization cycles;
5. They did not fully test whether there was a deposit-wide evolution in mineralized vein types, as suggested by previous studies (Cannell et al., 2005; Klemm et al., 2007);
6. They did not provide enough samples to complete a full comparative study with crystallization and alteration ages obtained for the deposit (Clark et al., 1983; Cuadra, 1986; Maksaev et al., 2004).

Here, we have dated 11 geologically constrained vein and breccia samples from several Mo-rich zones in order to address some of these limitations. By combining these results with field observations and additional geochronological evidence (Clark et al., 1983; Cuadra, 1986; Maksaev et al., 2004), this study provides further evidence for episodic intrusion emplacement and mineralization at El Teniente, involving at least three major pulses of magmatism and related hydrothermal activity.

Deposit Geology

Geologic setting

The tectonic setting, regional geology, and magmatic-hydrothermal evolution of El Teniente have been the focus of numerous studies over the last 90 years (Lindgren and Bastin, 1922; Howell and Molloy, 1960; Mann, 1975; Charrier et al., 2002; Skewes et al., 2002; Maksaev et al., 2004, 2009; Cannell et al., 2005, 2007; Klemm et al., 2007; Skewes and Stern, 2007; Rabbia et al., 2009; Astudillo et al., 2010; Stern et al., 2010; Vry et al., 2010; Muñoz et al., 2012). Combined, these investigations have helped build an understanding of the magmatic and hydrothermal evolution of the deposit.

El Teniente is hosted within the Teniente Mafic Complex (Fig. 2), a thick package of mafic sills, stocks, and volcaniclastic rocks of andesitic-basaltic composition (Howell and Molloy, 1960; Maksaev et al., 2004; Cannell et al., 2005; Stern et al., 2010; Vry et al., 2010). This complex was emplaced between 15.2 and 7.5 Ma, forming a >50-km$^3$ laccolith within the >2.5-km-thick Miocene Farellones Formation (Lindgren and Bastin, 1922; Cuadra, 1986; Skewes et al., 2002, 2005). At approximately 7.0 Ma, crustal thickening led to the termination of volcanism in the Southern volcanic zone (Fig. 1) and the inferred formation of a large magma chamber beneath El Teniente. The large volumes of water, sulfur, chlorine, and Cu present at El Teniente indicate a mantle-derived parental magma body, contaminated by altered oceanic crust and sediments, with a likely volume exceeding 600 km$^3$ (Stern, 1959, 1991; Cloos, 2001; Richards, 2003; Skewes et al., 2005; Skewes and Stern, 2007).

Deposit formation

Between 6.5 and 4.5 Ma, temperature fluctuations and magma mixing are thought to have led to the buoyant rise and emplacement of a series of felsic-intermediate intrusions (Clark et al., 1983; Cuadra, 1986; Skewes et al., 2002; Maksaev et al., 2004; Cannell et al., 2005; Vry et al., 2010). The Sewell Quartz Diorite is the oldest intrusion and makes up the southeastern quadrant of the mine area (Fig. 2). This is intruded by the A-Porphyry, the first extensively mineralized intrusion, on its northern margin. Although displaying a porphyritic texture, the A-Porphyry is an igneous breccia consisting of abundant Teniente Mafic Complex and Sewell Quartz Diorite clasts within an altered matrix of biotite, K-feldspar, plagioclase, anhydrite, and quartz (Cannell, 2004; Vry et al., 2010). SHRIMP U-Pb zircon dating of the Sewell Quartz Diorite and the A-Porphyry yielded a range of ages between 6.9 and 5.7 Ma (Maksaev et al., 2004; Fig. 3). Maksaev et al. (2004) stated that zircon ages from these units display bimodal distributions with dominant peaks occurring at 6.15 ± 0.08 and 6.46 ± 0.11 Ma and subordinate peaks at 5.59 ± 0.17 and 5.67 ± 0.19 Ma, respectively. This bimodality was recognized within individual zircon crystals, suggesting that two distinct crystallization events are recorded. Based on these data and the fact that the A-Porphyry cuts the Sewell Quartz Diorite, it was suggested that the younger peaks in zircon ages may represent the final crystallization of the A-porphyry, whereas the older ages may represent the crystallization of Sewell Quartz Diorite. The range of U-Pb dates recorded within this unit (Fig. 3) led to the suggestion that the Sewell Quartz Diorite is a composite intrusion in which the separate intrusion boundaries are masked by subsequent phases of potassic and quartz-sericite alteration (Maksaev et al., 2004).

The formation of the A-Porphyry was succeeded by the emplacement of a series of diorite pipes (Southern Diorite, Central Diorite, North-Central Diorite, and Northern Diorite) and the Grueso Porphyry to the north and west (Fig. 2). These intrusions have porphyritic textures and contain 35 to 70% phenocrysts of feldspar, amphibole, and biotite in a fine-grained aplite matrix of quartz, plagioclase, and minor K-feldspar. To date, only the Northern and Central diorites have been dated using U-Pb zircon methods (Maksaev et al., 2004). Based on Tera-Wasserburg concordia plots (Tera and Wasserburg, 1972) and weighted average age plots of U-Pb isotope data, omitting any anomalous outliers, Maksaev et al. (2004) concluded that zircons from the Northern and Central diorites also exhibit a clear bimodality with dominant peaks at 6.11 ± 0.13 and 6.25 ± 0.16 Ma and subordinate peaks at 5.48 ± 0.19 and 5.50 ± 0.24 Ma, respectively. The younger groups were interpreted to be the result of lead loss and/or zircon overgrowths. This is in accordance with previous studies which demonstrated that the U-Pb zircon system is prone to...
to partial resetting by postcrystallization hydrothermal fluids (e.g., Geisler et al., 2001). As a result, the crystallization of the diorite intrusions was interpreted to have occurred broadly synchronously at approximately 6.0 Ma with a hydrothermal overprint event at approximately 5.5 Ma (Maksaev et al., 2004).

The Teniente Dacite Porphyry was the final major intrusion associated with mineralization at El Teniente. This large, dike-like body displays sharp variations in mineral proportions and grain size that indicate multiple intrusive phases (Ossandón, 1974; Duarte, 2000; Rojas, 2002, 2003; Skewes et al., 2002; Maksaev et al., 2004; Cannell et al., 2005; González, 2004).
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2006; Hitschfeld, 2006) as well as veins truncated by igneous contacts (Vry et al., 2010). With the omission of two anomalous U-Pb zircon age determinations, produced by the dating of an older zircon antecryst and an anomalously young zircon that had possibly undergone significant lead loss, Maksaev et al. (2004) calculated a weighted average $^{206}\text{Pb}/^{238}\text{Pb}$ age of 5.28 ± 0.10 Ma for the Teniente Dacite Porphyry. However, U-Pb zircon ages and $^{40}\text{Ar}/^{39}\text{Ar}$ biotite and sericite ages for the Teniente Dacite Porphyry span >1 m.y. (Fig. 3) and appear to be polymodal, consistent with the petrological evidence for multiple phases of crystallization and alteration.

The Teniente Dacite Porphyry is cut by the Braden Breccia Pipe, which dominates the center of the deposit (Fig. 2). Several authors suggested that this rock-flour breccia formed between 4.7 and 4.6 Ma (e.g., Cannell et al., 2005) and that it may have marked the termination of significant shallow-level mineralization (e.g., Cuadra, 1986). In contrast, Maksaev et al. (2004) proposed that the Braden Breccia Pipe is a syn-mineralization diatreme that formed at approximately 4.8 Ma and was succeeded by significant Mo and Cu mineralization. This interpretation was based on U-Pb zircon ages from a mineralized dacite ring dike encircling the Braden Breccia Pipe, which displayed a unimodal distribution of spot ages with a weighted average of 4.82 ± 0.09 Ma.

A number of magmatic and hydrothermal breccias are found cutting and enveloping all the porphyry intrusions previously described (Fig. 2). These include igneous-, biotite-, anhydrite-, tourmaline-, and anhydrite-carbonate ± gypsum–cemented breccias (Vry et al., 2010; see Fig. 4). Actinolite-, magnetite-, K-feldspar-, and quartz-cemented breccias have also been described locally at the deposit (e.g., Skewes et al., 2002; Seguel et al., 2006; Vry et al., 2010). With the exception of early igneous breccias, all other breccia types are believed to be petrogenetically linked to vein stages that display mineralogy similar to that

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**FIG. 3.** Compiled geochronology for the crystallization of intrusions and molybdenite mineralization at El Teniente. (A) Intrusion crystallization, biotite, and sericite alteration (Quirt, 1972; Clark et al., 1983; Cuadra, 1986; Maksaev et al., 2004). Intrusions are listed in order of formation as reported in previous studies (Maksaev et al., 2004; Cannell et al., 2005; Vry et al., 2010). Histograms show temporal distribution of previously collected U-Pb zircon ages (Maksaev et al., 2004) divided into 0.1-m.y. intervals and ignoring any clearly anomalous outliers. $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating and total fusion ages are combined. (B) Re-Os molybdenite ages for vein types collected in two previous studies (Cannell, 2004; Maksaev et al., 2004). Vein types are given according to the vein classification scheme of Vry et al. (2010). For intrusion and Re-Os sample locations, refer to Figure 2.
of the breccia cements, and comparable alteration envelopes (Vry et al., 2010). However, distinct geochronological or fluid chemical evidence for these links has yet to be documented.

The zones of intense stockwork veining surrounding intrusion-breccia complexes at El Teniente are interpreted to represent the primary control on grade distribution (e.g., Maksaev et al., 2004, 2009; Vry et al., 2010). Three vein chronologies have been formulated using vein crosscutting relationships, each identifying at least 13 distinct vein types (the El Teniente mine classification used since 2003; Cannell et al., 2005; Vry et al., 2010). In this study, the vein chronology of Vry et al. (2010) was adopted (Fig. 5). This sequence is interpreted to be applicable across the deposit and is divided into three paragenetic stages: (1) the premineralization stage, associated with potassic alteration (K-feldspar alteration and biotitization); (2) the main mineralization stage, consisting of quartz and/or anhydrite veins with alteration halos grading from minor potassic (type 5) to none (6a–7b) to sericitic (type 8); (3) the late mineralization stage, consisting of veins containing tournaline and sulfosalts, possibly related to the formation of the Braden Breccia Pipe and its marginal breccia facies. Vein and breccia crosscutting relationships reported by

![Fig. 4. A–J. Magmatic and hydrothermal breccia types observed at El Teniente. (A) Igneous breccia showing angular Teniente Mafic Complex (TMC) clasts in a quartz-feldspar matrix (1754-127.1). (B) Plane-polarized light photomicrograph of a biotite breccia sample proximal to the A-Porphyry with 2- to 5-mm-long biotite laths in a fine biotite-quartz matrix (sample Bt Bx 1). (C) Early (premineralization stage) barren tournaline-cemented crackle breccia sampled at a shallow mine level to the east of the Braden Breccia Pipe (1754-317.5). (D) Anhydrite-cemented breccia associated with the carapace of the Southern Diorite at shallow mine levels (2083-262.2). (E) Quartz-cemented breccia with minor K-feldspar and anhydrite in matrix surrounding clasts of the North-Central Diorite (2215-49.8). Molybdenite mineralization predominantly occurs at the clast-matrix boundary. (F) Late mineralization-stage tournaline-cemented breccia to the east of the Braden Breccia Pipe, consisting of a molybdenite-rich matrix supporting highly altered diorite and Teniente Mafic Complex clasts (1754-285.9). (G) Marginal tournaline breccia with tournaline + molybdenite cement, found at the western rim of the Braden Breccia Pipe (2672-92.35). (H) Anhydrite-carbonate- and minor gypsum-cemented breccia supporting abundant bornite-chalcopyrite-molybdenite mineralization found in the southern section of the mine area (2672-103.05). (I) Braden Breccia sample containing subangular to rounded clasts of several different lithologies in a rock-flour matrix that contains fragmented chalcopyrite (2716-72.0). (J) Oxidized and altered hand specimen of the marginal breccia within the western rim of the Braden Pipe (2716-75.5). Matrix is molybdenite rich with minor chalcopyrite oxidized to malachite. Scale bars = 1 cm in length.](image-url)
Vry et al. (2010) are consistent across the deposit, with only rare reverse crosscutting relationships reported. However, it is unclear whether this is due to the synchronous development of each vein type across the deposit or the diachronous development of similar, localized vein halos surrounding each intrusion. In addition, even though crosscutting relationships are consistent, the exact relationship of each vein type with the others remains poorly understood, and as a result it is unclear whether any vein types developed coevally or cosparically, grading from one type into the other.

The vein chronology of Vry et al. (2010) was adopted, as it is the only classification scheme that presents a clear distinction between Mo-rich type 6a and 7a veins and chalcopyrite-bearing type 6b and 7b veins (Fig. 5). This detail is imperative in order to understand the decoupled nature of Mo and Cu mineralization. Molybdenite is recognized as an important vein mineralization.
constituent in eight of the 13 vein stages reported (Fig. 5). These include type 3 premineralization-stage veins, type 6a, 6b, 7a, and 8 main mineralization-stage veins, and type 9 and 10 late mineralization-stage veins. With the exception of type 7a veins, chalcopyrite is reported in all of these vein stages, but in highly variable proportions, thus suggesting a significant overlap in Mo and Cu mineralization. Vry et al. (2010) suggested that type 7 and 8 veins are the most important veins in terms of both Cu and Mo grade distributions.

Of the eight molybdenite-bearing vein stages identified, six vein types (or their inferred associated breccias) have been previously dated using the Re-Os molybdenite geochronometer (Figs. 2, 3). These samples reveal a range of mineralization ages spanning a 1.9-m.y. period (Cannell, 2004; Maksaev et al., 2004). Maksaev et al. (2004) suggested that there were five distinct episodes of mineralization at 6.30 ± 0.03, 5.60 ± 0.02, 5.01 to 4.96, 4.89 ± 0.05 to 4.78 ± 0.03, and 4.42 ± 0.02 Ma. Nine additional Re-Os molybdenite ages reported by Cannell (2004) correlate well with these pulses and also display an apparent younging with paragenetic stage (Fig. 3). The similarity in the results of these two studies and the interpreted close synchronicity of molybdenite mineralization with U-Pb zircon ages for the A-Porphyry, Diorites, Teniente Dacite Porphyry, and the Braden Breccia Pipe (Fig. 3) led to the conclusion that mineralization was closely associated with the formation of each of these intrusive units (Cannell, 2004; Maksaev et al., 2004; Cannell et al., 2005). However, the vein formation sequence has been interpreted as a deposit-wide evolution (e.g., Cuadra, 1986; Arévalo and Floody, 1998; Klemm et al., 2007), with, for example, early-stage veins only being associated with the oldest intrusions (Cannell et al., 2005). This may explain the lack of reverse crosscutting vein and breccia relationships.

To date, almost all dated molybdenite samples have come from one shallow section across the northern part of the deposit and from the carapace of the A-Porphyry (Fig. 2). As a result, there is uncertainty regarding the timing of molybdenite mineralization across the entire deposit. In addition, the apparent deposit-wide evolution in vein paragenesis may be misleading because the oldest Mo-mineralized vein stages analyzed (type 5) were obtained from the oldest intrusions (the Sewell Quartz Diorite and the A-Porphyry) whereas the youngest veins and breccias analyzed (type 8 and 10) were spatially associated with the younger Teniente Dacite Porphyry and Braden Breccia Pipe (Figs. 2, 3). As a result, these data alone cannot distinguish between a deposit-wide evolution in vein and breccia type (e.g., Cannell et al., 2005; Klemm et al., 2007) or a history involving multiple hydrothermal cycles (e.g., Maksaev et al., 2004; Vry et al., 2010; Astudillo et al., 2010).

**Grade distributions**

In order to identify the most important controls of Mo distribution and the extent of Mo-Cu decoupling at El Teniente, deposit geology (Fig. 2) was compared with combined Mo and Cu grade distribution data (courtesy of Codelco Division El Teniente) for three mine levels (1,890 m, Fig. 6; 2,200 m, Fig. 7; and 2,350 m above sea level [masl], Fig. 8). Due to sloping topography, the current land surface is 2,300 masl at the western margin of the deposit area and approximately 3,300 masl on the eastern margin. Morphological reconstruction of a nearby volcanic center (Rivera and Falconcón, 1998), estimates of local exhumation rates (Skewes and Holmgren, 1993; Kurtz et al., 1997), and calculations of pressure using fluid inclusions (Cannell, 2004) indicate approximately 2,000 m of erosion at El Teniente since approximately 5 Ma. Therefore, the deepest grade distribution slice examined is inferred to represent a depth of approximately 3 km below the paleosurface.

At the deepest mine level studied, Mo mineralization displays a close spatial association with the Northern, North Central, and Central diorites (Fig. 6). Mineralization is abundant within and surrounding these diorites, with the highest grades observed at their contacts with the Teniente Mafic Complex. Copper grades also show a clear spatial relationship with these intrusions, with the 1.0 wt % Cu contour surrounding all the diorite intrusions and enclosing zones of maximum Mo grade. High Mo and Cu grades also appear to show a relationship with igneous and anhydrite breccias surrounding the Northern Diorite and North-Central Diorite and also to the south of the Braden Breccia Pipe. Particularly high Mo-Cu ratios are found on the western and southern sides of the Braden Breccia Pipe and proximal to the Southern Diorite. At this level, the center of the Braden Breccia Pipe, the Teniente Dacite Porphyry, and A-Porphyry all show relatively low Cu and Mo grades (Fig. 6).

At intermediate mine levels, the high-grade Mo and Cu shells spatially associated with the Northern, North Central, and Central diorites shift approximately 100 m to the west (Fig. 7), maintaining a separation similar to that observed at 1,890 masl. This is likely to be a manifestation of the orientation of the diorite pipes, which tilt slightly toward the northwest (e.g., Vry et al., 2010). The highest Mo grades are associated with the western and eastern rims of the Braden Breccia Pipe, with an additional Mo anomaly occurring within a tourmaline breccia south of the Braden Breccia Pipe, which is cut by the southern tip of an NW-trending latite dike. Highest Cu grades are associated with the southern tip of the North Central Diorite and the northern tip of the Central Diorite (Fig. 7). Elevated Cu grades also occur at the margins of the Teniente Dacite Porphyry, in particular associated with a large anhydrite breccia body to the north of the Braden Breccia Pipe, where grades exceed 2 wt %.

At the shallowest mine level studied (2,350 masl), both Mo and Cu are concentrated within and surrounding the A-Porphyry, Southern Diorite, North Central Diorite, and Northern Diorite (Fig. 8). Unlike Cu, high-grade Mo mineralization also occurs in a semicontinuous halo of >0.03 wt % approximately 100 to 250 m from the perimeter of the Braden Breccia Pipe. This enriched halo appears to be a continuation of that seen at the intermediate mine level (Fig. 7) and occurs outboard of the marginal tourmaline breccias that surround the breccia pipe. High Mo grades are also observed in association with small tourmaline breccia bodies at the southern tip of the latite dike southwest of the Braden Breccia Pipe and overlying the Grueso Porphyry (Fig. 8). Zones of high Cu grade are found to the north of the Braden Breccia Pipe and extend to the north and east, where they display a spatial association with the North Central Diorite and the margins of the Teniente Dacite Porphyry. The Mo halo surrounding the
Braden Breccia Pipe is associated with dilution of Cu grades associated with the Teniente Dacite Porphyry margins (Fig. 8).

**Methodology**

*Drill core logging*

Fieldwork was completed at El Teniente in two visits in October–November 2011 and September–October 2012. Fourteen drill cores were studied in order to analyze mineralization and hydrothermal alteration assemblages associated with intrusions and breccias at various mine levels (see Table 1; Fig. 2). Over 240 samples were collected for laboratory analysis. These included examples of each vein and breccia type hosted by different lithologies, samples suitable for fluid inclusion analysis, and well-constrained, Mo-rich samples for Re-Os dating.

Based on Mo grade distribution maps, six drill cores were selected on which to complete detailed vein distribution analyses. These formed three, near-horizontal, E-W–trending transects that cut the diorites at various depths (transects 1–3) and a final transect (transect 4) that cuts the Mo-rich halo and Teniente Dacite Porphyry to the south of the Braden Breccia Pipe (Fig. 2). Detailed notes on lithology, alteration, and sulfide abundances were taken along each transect and the total number of veins of each type was recorded for each meter interval following the vein classification of Vry et al. (2010). The lack of reverse crosscutting veins and breccia relationships surrounding these intrusions (Vry et al., 2010) suggest that the main mineralization-stage vein halos in transects 1 to 4 are not likely to be formed by the overprinting of veins related to multiple mineralization events. This means that the vein distribution analysis either should record overall vein abundances for a deposit-wide evolution in vein type or will allow for the study of vein abundances surrounding essentially isolated mineralized centers.

Near-horizontal transects were selected in order to intersect veins surrounding the diorites and Braden Breccia Pipe that were previously described as being predominantly vertical or subvertical (e.g., Cannell et al., 2005). The majority of veins present in transects 1 to 4 cut the drill cores at near-perpendicular angles, rarely extending for lengths of >6 cm, and

![Fig. 6. Grade distribution map of Mo and Cu (wt %) at a deep mine level (1,890 masl). Outline map from Figure 2 is superimposed to show the relationship between mineralization and geology. Original maps, Mo grades, and Cu grades courtesy of CODELCO Division El Teniente.](image-url)
are therefore predominantly oriented roughly north-south. In the rare cases where veins ran along the drill core for >10 cm or branched into two separate veins, each with lengths of >3 cm, they were recorded as two veins based on the assumption that they would exert a higher than normal control on Mo and Cu grades in their drill core interval. Composite veins were counted as two separate veins, provided the separate vein generations could be identified. If this was not possible, the vein was classified by its predominant mineralogy. Due to the relatively uniform thickness of each vein type (discussed in subsequent sections) and the fact that the thickest veins are typically gangue dominated (e.g., early barren quartz and anhydrite veins and late gypsum veins), vein width was not taken into account. However, notes were made when unusually large, sulfide-rich veins were encountered. Veinlets with widths of <1 mm were not recorded. Results were compared against average Mo and Cu grades provided by CODELCO División El Teniente. Average grades are reported for 6-m drill core intervals along transects 1 and 2 whereas grades are given for 20-ft intervals along the earlier studied drill cores in transects 3 and 4.

In order to investigate the distribution of Mo with depth, two drill cores (DDH 1805 and DDH 1034) were selected in order to provide a near-vertical section proximal to the North-Central Diorite (Fig. 2, Table 1). These extended down to an elevation of 1,300 masl, representing a vertical profile of approximately 1 km that extends down to an estimated paleodepth of 3.5 to 4.0 km. Six additional drill cores were studied to enable a deposit-wide analysis of molybdenite mineralization by assessing crosscutting relationships between vein types, breccias, and intrusions and their association with Mo or Cu anomalies (Table 1).

Petrography

Representative and well-constrained vein and breccia samples from several intrusions and the Teniente Mafic Complex were selected for petrographic analysis. These samples were obtained from a range of depths and had highly contrasting sulfide abundances and associated alteration. Sixty polished thin sections were prepared with thicknesses of 32 to 150 µm. All samples were studied using conventional transmitted light petrography to confirm vein/breccia classifications and by

![Grade distribution map of Mo and Cu (wt %) at an intermediate mine level (2,170 masl). Outline map from Figure 2 is superimposed to show the relationship between mineralization and geology. Original maps, Mo grades, and Cu grades courtesy of CODELCO Division El Teniente.](image)
DISTRIBUTION AND TIMING OF MOLYBDENITE MINERALIZATION AT EL TENIENTE, CHILE

Fig. 8. Grade distribution map of Mo and Cu (wt %) at a shallow mine level (2,350 m asl). Outline map from Figure 2 is superimposed to show the relationship between mineralization and geology. Original maps, Mo grades, and Cu grades courtesy of CODELCO Division El Teniente.

Table 1. Summary Information for Drill Cores Analyzed During This Study

<table>
<thead>
<tr>
<th>Drill core</th>
<th>Starting coordinates</th>
<th>Azimuth</th>
<th>Inclination</th>
<th>Meters studied</th>
<th>Elevation masl</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>DDH 2371 N 942.535 E 940.844</td>
<td>89.0°</td>
<td>-4°</td>
<td>0–200</td>
<td>2,055.34</td>
<td>TMC-ND</td>
</tr>
<tr>
<td>DDH 2363</td>
<td>N 942.041 E 921.731</td>
<td>270.6°</td>
<td>-6°</td>
<td>0–200</td>
<td>2,054.28</td>
<td>ND-TMC</td>
</tr>
<tr>
<td>T2</td>
<td>DDH 2215 N 505.017 E 1115.823</td>
<td>90.0°</td>
<td>+15.3°</td>
<td>0–200</td>
<td>1,987.88</td>
<td>TMC-NCD</td>
</tr>
<tr>
<td>DDH 2230</td>
<td>N 505.062 E 1108.458</td>
<td>269.8°</td>
<td>-3.2°</td>
<td>0–200</td>
<td>1,986.40</td>
<td>NCD-TMC</td>
</tr>
<tr>
<td>T3</td>
<td>DDH 2083 N 199.930 E 1380.040</td>
<td>270.0°</td>
<td>+2°</td>
<td>0–300</td>
<td>2,214.24</td>
<td>TMC-CD-SD</td>
</tr>
<tr>
<td>DDH 1888</td>
<td>S 413.420 E 423.420</td>
<td>74.0°</td>
<td>-52°</td>
<td>0–300</td>
<td>2,283.21</td>
<td>TMC</td>
</tr>
<tr>
<td>T4</td>
<td>DDH 1805 N 602.511 E 1209.048</td>
<td>Vertical</td>
<td>-90°</td>
<td>0–533</td>
<td>1,984.84</td>
<td>NCD-TMC</td>
</tr>
<tr>
<td>DDH 1034</td>
<td>N 619.285 E 1353.062</td>
<td>265°</td>
<td>-50°</td>
<td>0–590</td>
<td>2,286.64</td>
<td>NCD-TMC</td>
</tr>
<tr>
<td>DDH 2638</td>
<td>N 1315.955 E 252.325</td>
<td>44.91°</td>
<td>-54.8°</td>
<td>0–300</td>
<td>2,166.72</td>
<td>TMC-TDP</td>
</tr>
<tr>
<td>DDH 1754</td>
<td>N 318.659 E 933.357</td>
<td>87°</td>
<td>-10.00</td>
<td>0–390</td>
<td>2,384.00</td>
<td>TMC-CD</td>
</tr>
<tr>
<td>DDH 2305</td>
<td>N 36.786 E 1702.716</td>
<td>279.65°</td>
<td>-13.95°</td>
<td>0–390</td>
<td>2,322.62</td>
<td>AF-TMC</td>
</tr>
<tr>
<td>DDH 2561</td>
<td>N 750.194 E 188.325</td>
<td>269.35°</td>
<td>-59.17°</td>
<td>60–360</td>
<td>2,164.83</td>
<td>TMC-TDP</td>
</tr>
<tr>
<td>DDH 2672</td>
<td>S 775.516 E 565.298</td>
<td>270.67°</td>
<td>+28.90°</td>
<td>0–190</td>
<td>2,192.81</td>
<td>TB-LD-TMC</td>
</tr>
<tr>
<td>DDH 2716</td>
<td>S 61.438 E 120.059</td>
<td>77.0°</td>
<td>+34.00°</td>
<td>0–120</td>
<td>2,356.23</td>
<td>TMC-BB</td>
</tr>
</tbody>
</table>

Notes: For drill core locations refer to Figure 2.
Abbreviations: AP = A-Porphyry, BB = Braden Breccia Pipe, CD = Central Diorite, LD = Latite Dike, NCD = North-Central Diorite, ND = Northern Diorite, SD = Southern Diorite, T1–T4 = Transects 1–4, used for vein distribution analysis, TB = Tourmaline Breccia, TDP = Teniente Dacite Porphyry; TMC = Teniente Mafic Complex.
reflected light microscopy in order to identify sulfides present, their relative abundances, and their timing relationships.

**Geochemistry**

Unlike the other dating techniques used at El Teniente, which may be susceptible to the effects of hydrothermal overprinting, the Re-Os isotopic system displays closed behavior during postmineralization alteration, ductile deformation, and regional metamorphism (e.g., Stein et al., 1998; Selby and Creaser, 2001; Stein and Bingen, 2002; Bingen and Stein, 2003; Ootes et al., 2007; Bingen et al., 2008; Lawley and Selby, 2012). This, combined with the fact that molybdenite is the third most abundant ore mineral at El Teniente (Camus, 1975), makes it a suitable technique for dating mineralization. Twenty samples were initially selected for Re-Os molybdenite dating based on their vein/breccia type, sample depth, and geographic locations. Large composite veins and overprinted veins were avoided so that accurate age determinations could be made for single molybdenite generations in each vein. Consistent with their premineralization-stage classification, reflected light analysis revealed that the amount of molybdenite in all selected type 3 to 4b veins was either insufficient for dating or it was the result of overprinting by later vein generations. As a result, no samples from this paragenetic stage were dated in this study.

Eleven samples were selected for Re-Os molybdenite dating, comprising seven main mineralization-stage samples and four samples from the late mineralization stage. Vein samples ranging from type 6a to type 10 were obtained from proximal to the Central Diorite and Southern Diorite in order to study the temporal evolution of veins within a single part of the deposit (Fig. 2). Two type 6a vein samples with a difference in elevation of approximately 550 m were selected proximal to the North-Central Diorite in order to ascertain the relationship between depth and timing of molybdenite mineralization (1034-837.0, 2215-119.9). Additional samples analyzed included a molybdenite-rich tourmaline breccia from the western rim of the Braden Breccia Pipe (2716-8.0) and a type 6b vein associated with the southern tip of the Teniente Dacite Porphyry (1888-133.8). The final sample analyzed was a sample from the B-fault, an anastomosing NW-trending fault zone that coincides with a significant Mo anomaly to the east of the Braden Breccia Pipe (Figs. 2, 8). Mine geologists report evidence for right-lateral, strike-slip displacement along this fault zone, which has created slickensides on the contained molybdenite. Although this indicates displacement following molybdenite mineralization, the timing of Mo introduction remains untested.

This information can be used to assess the relationships between fault activation, intrusion emplacement, and crystallization and mineralization.

All samples were prepared and analyzed at the University of Alberta Radiogenic Isotope Facility, Canada, using the method of Selby and Creaser (2001, 2004). Veins and breccia zones of interest were cut out of each sample to create molybdenite-rich specimens with weights of <20 g. Cut samples were crushed separately using a porcelain disk mill, collecting the fraction that passed through a 200–70 mesh sieve. Molybdenite was then separated using a Frantz isodynamic magnetic separator and heavy liquid (methyleniodide). Due to the low abundance of molybdenite in sample 2083-184.1, molybdenite was separated using the hydrofluoric acid (HF) chemical separation technique of Lawley and Selby (2012) to maximize recovery. Lawley and Selby (2012) showed that this technique does not affect the Re and Os isotope composition of molybdenite and can be used to obtain accurate and reproducible age determinations for ultrafine molybdenite.

Previous Re-Os studies have shown that analyzing large amounts of separated or handpicked molybdenite (i.e., 10 mg) or small aliquots of separated molybdenite (<1 mg) can both yield dates that significantly deviate from “true” sample ages (Stein et al., 1998, 2001; Creaser and Selby, 2002). In order to avoid anomalous results produced by the sampling of multiple generations of molybdenite, relatively small aliquots of molybdenite with weights of approximately 1.2 mg were separated. These were accurately weighed and dissolved together with a known amount of “mixed-double” spike (188Os + 190Os + 185Re; Markey et al., 2007) in a thick-walled Carius tube. Os and Re were separated using a combination of solvent extraction, microdistillation, and anion chromatographic methods and analyzed by N-TIMS using a Thermo Triton mass spectrometer and Faraday collectors. Previous studies have shown this to be an effective technique for deriving highly precise, accurate, and reproducible molybdenite ages (Selby and Creaser, 2001, 2004; Stein et al., 2001). Procedural blanks are less than 2 pg for Re and 3 pg for Os, and model ages were calculated using the 187Re decay constant of 1.666 × 10–11a–1 (Smoliar et al., 1996). Uncertainty in the Re-Os model ages includes uncertainty in the 187Re decay constant, Re and Os concentrations as a result of weighing uncertainties (spikes and samples), spike calibration, and mass spectrometry analytical uncertainties. All age uncertainties are reported at the 2σ level in the results section. Three samples were selected for replicate runs using the same mineral separate in order to assess the accuracy and reproducibility of results and confirm that these samples comprised of a single generation of molybdenite.

**Breccia Distribution and Petrography**

Seven breccia types were observed in this study (igneous-, biotite-, anhydrite-, quartz-, tourmaline-, anhydrite-carbonate ± gypsum–cemented, and rock-flour breccias). These are spatially associated with different intrusions and contain highly variable sulfide abundances, as summarized in Table 2. Consistent with their interpreted premineralization timing (Canell et al., 2005; Vry et al., 2010), Mo and Cu sulfides are rare in igneous and biotite breccias. However, all other breccias contain highly variable, and often appreciable, amounts of Cu (5%–40%) and Mo sulfides (5%–20%). Mineralization in anhydrite breccias is often concentrated where later Mo- and Cu-rich veins cut the breccia matrix. However, in most cases, intergrown sulfide and gangue minerals are present in their matrices, and so mineralization is interpreted to have been synchronous with formation.

In transects 1 to 4, igneous-, anhydrite-, tourmaline-, and anhydrite-carbonate ± gypsum–cemented breccias were observed. Anhydrite breccias commonly form a shell surrounding the diorite pipes and contain elevated average Mo and Cu grades in transects 1, 3, and 4 (Table 3A, B). However, average grades
were lower in intervals of anhydrite breccia in transect 2, reflecting the locally variable sulfide abundances within their cements (Table 2).

Tourmaline- and anhydrite-carbonate ± gypsum–cemented breccias are abundant at shallow mine levels, where they cut all intrusions and truncate type 8 veins (e.g., Fig. 9A). Mo-rich tourmaline breccias are particularly abundant surrounding the Braden Breccia Pipe, where 6-m drill core intersections have average Mo grades of up to 0.35 wt % (DDH 2716). In these breccias, fine-grained Mo often occurs throughout the tourmaline-dominated matrix. Mo-poor tourmaline breccias were also observed. These principally occur at deeper mine levels and in distal positions relative to the Braden Breccia Pipe. Intersections of tourmaline breccia are generally Cu poor (Table 3B), although sections of chalcopyrite- and pyrite-rich tourmaline breccias were observed in transect 1 and in drill cores DDH 2716, 1888, and 2672. Anhydrite-carbonate ± gypsum–cemented breccias are almost always enriched in Mo (e.g., Table 3A). Molybdenite is predominantly concentrated around clast margins, where it commonly occurs as large bladed crystals. Cu grades are generally low in anhydrite-carbonate ± gypsum–cemented breccias (Table 3B). However, some shallow-level anhydrite-rich examples contain significant chalcopyrite and bornite infill, accounting for the highly variable average Cu grades recorded (0.98–1.93 wt %) for the transects studied (Table 3B). In some cases, Cu sulfide mineralization occurs alongside significant molybdenite in the breccia matrix (e.g., Fig. 9B, C). This suggests that some late-stage pulses of both Mo- and Cu-rich hydrothermal fluids occurred.

Table 2. Summary of the Observed Compositions, Occurrences, and Key Petrographic Features of the Seven Different Breccia Types Observed During Drill Core Logging

<table>
<thead>
<tr>
<th>Breccia Type</th>
<th>Composition</th>
<th>Occurrence</th>
<th>Sulfides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Igneous</td>
<td>Plag phenocrysts + bt-gz-anh</td>
<td>Second most common breccia type observed</td>
<td>Typically contain &lt;1% mo, &lt;2% cpy, &lt;1% py, and no bo</td>
</tr>
<tr>
<td></td>
<td>Clasts = predominantly TMC ± Sewell</td>
<td>Occur surrounding every intrusion at all mine levels, suggesting that they are linked to the emplacement of each intrusion</td>
<td>Sulfides interpreted to be the result of later vein stages and disseminations related to the main and late mineralization stages</td>
</tr>
<tr>
<td></td>
<td>Quartzite + A-Porphyry +</td>
<td>Cut by all vein stages from 3 onward and all other breccias</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diorite, Teniente Dacite Porphyry</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biotite</td>
<td>Plag phenocrysts + bt-gz-anh</td>
<td>Only observed proximal to the A-Porphyry and SQD in DDH 2305; none observed in other intrusions</td>
<td>Minor cpy &lt;3% observed in one sample (Bt Bx 1)</td>
</tr>
<tr>
<td></td>
<td>Clasts = predominantly TMC ± SQD</td>
<td>Sample bt bx 1 was a supplementary sample obtained from a deep mine level where bt breccia preservation is inferred to be better</td>
<td>Opaque daughter minerals (cpy?) observed in large fluid inclusions</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anhydrite</td>
<td>Plag phenocrystals + bt-gz-anh</td>
<td>Most frequently observed breccia type during this study</td>
<td>Highly variable; typically &lt;5% mo, &lt;10% cpy, &lt;2% bo, &lt;5% py</td>
</tr>
<tr>
<td></td>
<td>Clasts = predominantly TMC ± A-Porphyry</td>
<td>Observed surrounding the A-Porphyry, diorites, and Teniente Dacite Porphyry</td>
<td>Contain up to 40% mo, typically found at the clast-matrix contacts</td>
</tr>
<tr>
<td></td>
<td>Quartzite + altered diorite</td>
<td>Teniente Dacite Porphyry; notable sulfide-rich examples recorded proximal to the A-Porphyry, North-Central Diorite, Southern Diorite, and to the south of the Braden Pipe</td>
<td>Contain up to 50%Mo cpy found throughout anh cement</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>Qz with minor anh and K-fsp in some cases</td>
<td>Rare occurrences observed at the contacts of the diorites in areas of intense qz stockwork veining; best example observed proximal to the North-Central Diorite</td>
<td>Typically contain minor mo 5–10% (e.g., Fig. 4E), usually found at cement-clast contacts</td>
</tr>
<tr>
<td></td>
<td>Clasts = predominantly TMC and altered</td>
<td>Evidence that quartz is replaced by anh cement, possibly observed during the type 6 vein stage</td>
<td>Minor cpy &lt;5% in all samples observed</td>
</tr>
<tr>
<td></td>
<td>diorite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tourmaline</td>
<td>Tour ± anh, often with abundant mo</td>
<td>Observed surrounding the Braden Breccia Pipe in DDH 2716, DDH 2083, and DDH 1888 as well as cut by the latite dike to the south of the Braden Pipe (DDH 2672)</td>
<td>Highly variable with examples containing 0–70% Mo in cement</td>
</tr>
<tr>
<td></td>
<td>Clasts = Teniente Dacite Porphyry +</td>
<td>Crosscut the Teniente Dacite Porphyry and diorites and are cut by the Braden Pipe</td>
<td>Several examples contain abundant cpy and py, possibly representing sulfide zonation surrounding the Braden Pipe</td>
</tr>
<tr>
<td></td>
<td>TMC ± diorites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anhydrite–</td>
<td>Anh + chb ± gyp ± sulfosilts</td>
<td>Observed crosscutting the diorites and Teniente Dacite Porphyry in most drill cores</td>
<td>Typically contain abundant mo (5–50%) and bo (5–20%), which appear to be coprecipitated</td>
</tr>
<tr>
<td>carbonate ±</td>
<td>Clasts = Teniente Dacite Porphyry + TMC + diorites</td>
<td>Display an apparent spatial relationship with the presence of NW-trending and concentric faults surrounding the Braden Pipe (see Fig. 2)</td>
<td>Cpy &lt;10% in most samples</td>
</tr>
<tr>
<td>gypsum ±</td>
<td></td>
<td></td>
<td>Minor sulfosilts in several samples (tennantite + enargite)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock flour</td>
<td>Plag phenocrystals + bt-gz-anh</td>
<td>Rock-flour breccia composes the central portion of the Braden Pipe surrounded by the marginal tourmaline breccias</td>
<td>Shattered fragments of cpy and py with minor mo and bo in matrix</td>
</tr>
<tr>
<td></td>
<td>Clasts = All intrusions, TMC + brecciated tour and sulfides (cpy)</td>
<td>Recorded in drill cores DDH 2716 and at the start of DDH 1754</td>
<td>Cpy-rich clasts of Teniente Dacite Porphyry and diorite truncated by breccia matrix</td>
</tr>
</tbody>
</table>

Notes: Breccia names are derived from the primary components of cement/matrix; these are listed in an inferred idealized chronologic order proposed by Vry et al. (2010); for mineral abbreviations refer to Figure 5 caption; TMC = Teniente Mafic Complex.
The abundance and distribution of each vein type and its typical sulfide associations are summarized in Table 4. The vein distribution analysis recorded a total of 33,723 veins at an overall average frequency of ~24 veins per meter in transects 1 to 4. Nearly 80% of veins were related to the main mineralization stage, with approximately 10% belonging to each of the premineralization and late mineralization stages. Abundant sulfide mineralization was observed in every vein stage, with the exception of type 1 veins (Table 4). Of these, eight vein types (3, 5, 6a, 6b, 7a, 7b, 8, 9, and 10) commonly contain molybdenite and chalcopyrite that is observable without the use of a hand lens. Although often present in the same veins, evidence for the apparent coprecipitation of Mo and Cu was rarely observed. Thin section analysis reveals that molybdenite typically occurs on separate vein growth zones to chalcopyrite and bornite or is overprinted or truncated by later Cu sulfides.

Table 3. Summary of Grade Data for Drill Cores in Transects 1 to 4 Showing Average Mo (A) and Cu Grades (B) for Each Host Lithology

<table>
<thead>
<tr>
<th>A. Mo Grades</th>
<th>Veins</th>
<th>Grades</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Drill core</td>
<td>Common veins</td>
<td>Veins/m</td>
</tr>
<tr>
<td>T1</td>
<td>DDH 2371</td>
<td>6a &gt; 8 &gt; 6b</td>
<td>16.8</td>
</tr>
<tr>
<td>T2</td>
<td>DDH 2363</td>
<td>6b &gt; 8 &gt; 6a</td>
<td>21.9</td>
</tr>
<tr>
<td>T3</td>
<td>DDH 2215</td>
<td>6a &gt; 6b &gt; 8</td>
<td>17.4</td>
</tr>
<tr>
<td>T4</td>
<td>DDH 2230</td>
<td>6a &gt; 6b &gt; 8</td>
<td>22.5</td>
</tr>
<tr>
<td>Average all</td>
<td>DDH 2083</td>
<td>8 &gt; 6a &gt; 6b</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td>DDH 1888</td>
<td>9 &gt; 8 &gt; 6a</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.1</td>
</tr>
</tbody>
</table>

B. Cu Grades

<table>
<thead>
<tr>
<th>T</th>
<th>Drill core</th>
<th>Common veins</th>
<th>Veins/m</th>
<th>Average Cu</th>
<th>TMC</th>
<th>DIO</th>
<th>Teniente Dacite Porphyry</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>DDH 2371</td>
<td>6a &gt; 8 &gt; 6b</td>
<td>16.8</td>
<td>1.13</td>
<td>1.36</td>
<td>1.04</td>
<td>1.13</td>
</tr>
<tr>
<td>T2</td>
<td>DDH 2363</td>
<td>6b &gt; 8 &gt; 6a</td>
<td>21.9</td>
<td>1.19</td>
<td>1.20</td>
<td>1.32</td>
<td>1.17</td>
</tr>
<tr>
<td>T3</td>
<td>DDH 2215</td>
<td>6a &gt; 6b &gt; 8</td>
<td>17.4</td>
<td>1.20</td>
<td>1.33</td>
<td>0.86</td>
<td>1.17</td>
</tr>
<tr>
<td>T4</td>
<td>DDH 2230</td>
<td>6a &gt; 6b &gt; 8</td>
<td>22.5</td>
<td>0.92</td>
<td>0.92</td>
<td>0.63</td>
<td>0.89</td>
</tr>
<tr>
<td>T3</td>
<td>DDH 2083</td>
<td>8 &gt; 6a &gt; 6b</td>
<td>26.7</td>
<td>1.27</td>
<td>1.24</td>
<td>1.27</td>
<td>1.66</td>
</tr>
<tr>
<td>T4</td>
<td>DDH 1888</td>
<td>9 &gt; 8 &gt; 6a</td>
<td>33.3</td>
<td>0.99</td>
<td>0.96</td>
<td>0.85</td>
<td>1.39</td>
</tr>
<tr>
<td>Average all</td>
<td>DDH 2371</td>
<td>6a &gt; 8 &gt; 6b</td>
<td>16.8</td>
<td>1.13</td>
<td>1.36</td>
<td>1.04</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Notes: Common veins = three most common vein types recorded; grade data provided by CODELCO Division El Teniente
Abbreviations: A-C-G = anhydrite-carbonate ± gypsum breccias, Bx = Breccia, DIO = Diorite, T = Transect, TMC = Teniente Mafic Complex

Vein Distribution and Petrography

The abundance and distribution of each vein type and its typical sulfide associations are summarized in Table 4. The vein distribution analysis recorded a total of 33,723 veins at an overall average frequency of ~24 veins per meter in transects 1 to 4. Nearly 80% of veins were related to the main mineralization stage, with approximately 10% belonging to each of the premineralization and late mineralization stages. Abundant sulfide mineralization was observed in every vein stage, with the exception of type 1 veins (Table 4). Of these, eight vein types (3, 5, 6a, 6b, 7a, 7b, 8, 9, and 10) commonly contain molybdenite and chalcopyrite that is observable without the use of a hand lens. Although often present in the same veins, evidence for the apparent coprecipitation of Mo and Cu was rarely observed. Thin section analysis reveals that molybdenite typically occurs on separate vein growth zones to chalcopyrite and bornite or is overprinted or truncated by later Cu sulfides.

Total vein abundance is generally higher at shallower mine levels (e.g., Table 3A), largely due to increases in type 7b to
DISTRIBUTION AND TIMING OF MOLYBDENITE MINERALIZATION AT EL TENIENTE, CHILE

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**Type 7b Vein**
- Tenniente Dacite Porphyry
- Bladed molybdenite
- Tourmaline cement
- Chalcopyrite

**Type 7a Vein**
- Bladed molybdenite with chalcopyrite overprint
- Bladed molybdenite

**Type 6a Vein**
- Reopened quartz-molybdenite vein
- Reopen quartz-molybdenite vein
- Composite 6b vein with chalcopyrite overprint

**Composite 6b Vein with chalcopyrite overprint**
- Bladed molybdenite
- Anhydrite

**Type 9**
- Bladed molybdenite
- Chalcopyrite
- Minor molybdenite
- Anhydrite
- Minor chalcopyrite

**Type 10**
- Chalcopyrite
- Infilling microfractures
- Chalcopyrite veinlet
- Molybdenite
- Truncated mo and bo

**Gypsum Carbonate**
- Anhydrite
- Carbonate

**Quartz Vein**
- Tourmaline
- Molybdenite

**TMC**
- Molybdenite
- Tourmaline

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Table 4: Summary of the Mineralogy, Occurrences, and Typical Sulfide Abundances of Vein Types Observed in the 15 Studied Core Drills Displayed in Figure 2

<table>
<thead>
<tr>
<th>Vein Mineralogy Occurrences</th>
<th>N</th>
<th>Sulfides</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Bt-act ± (chl-cpy) No veins observed during study</td>
<td>0</td>
<td>None observed during this study</td>
</tr>
<tr>
<td>Rare occurrences at deep mine levels associated with the Sewell Quartz Diorite and Bt halo</td>
<td>324</td>
<td>Minor primary mo &lt;1% and cpy &lt;1% observed in this section only</td>
</tr>
<tr>
<td>2 Mag ± qz-anh- Preserved at depth and present as pervasive magnetic patches at shallow mine levels (&gt;2,200) in the TMC</td>
<td>59</td>
<td>Many replaced by cpy (5-15%) or py (5-15%)</td>
</tr>
<tr>
<td>Typical thicknesses of 5 to 10 mm Many replaced by cpy (5-15%) or py (5-15%)</td>
<td>59</td>
<td>Rare, thin biotite veins (&lt;2 mm) found in the A-Porphyry with extremely rare examples in the diorites 0.1%</td>
</tr>
<tr>
<td>3 Bt-qz ± anh- The most abundant premineralization stage vein, found throughout the TMC at all mine levels</td>
<td>59</td>
<td>Most contain 5-30% cpy-sulfides</td>
</tr>
</tbody>
</table>
10 vein frequency (Fig. 10). No vein type displays a clear increased abundance at deep mine levels, although the relative proportion of molybdenite-rich type 6a and 7a veins generally increases with depth in the two deepest drill cores studied (DDH 1805 and 1034). Vein frequencies are lower within the finger porphyries than within the mafic complex rocks immediately surrounding them. For example, an average vein frequency of 16.31 veins/meter was recorded for the Northern Diorite in transect 1, whereas the Teniente Mafic Complex exhibits a frequency of 21.96 veins/meter. This is largely due to pronounced decreases in the abundances of type 3 and 8 veins within the finger porphyries.

**Premineralization-stage veins**

Premineralization-stage veins are abundant within the Teniente Mafic Complex, the Sewell Quartz Diorite and, to a lesser extent, the A-Porphyry, but are extremely rare in the diorites and Teniente Dacite Porphyry. Of these, type 3 and 4a veins were the only abundant veins observed in transects 1 to 4 (Table 4). Type 3 veins have modal widths of approximately 8 mm and commonly contain abundant chalcopyrite and/or molybdenite (Table 4). Despite this, type 3 vein abundance shows no clear relationship with Mo and Cu grades in transects 1 to 4 (Fig. 11A-D). Type 3 vein abundance data fall in clusters with the Teniente Mafic Complex being typified by higher premineralization-stage vein abundances and a slight bias toward higher Cu grades relative to Mo (Fig. 11A, B). There is a weak negative correlation between type 3 vein abundance and Cu grades in the Teniente Mafic Complex (Fig. 11D), suggesting that these veins are not economically important in controlling grade distributions in transects 1 to 4.

Type 4a veins commonly have widths of <1 mm, accounting for their low abundance in the vein distribution analysis (Table 4). Reflected light analysis reveals that they typically contain <1% molybdenite and Cu sulfides that do not appear to be the product of overprinting. These low primary sulfide abundances confirm their previous categorization as premineralization-stage veins (Vry et al., 2010).

**Main mineralization-stage veins**

Main mineralization-stage veins occur throughout the Teniente Mafic Complex as well as within every intrusion at El Teniente. In accordance with previous studies (Camus, 1975; Cannell et al., 2005; Vry et al., 2010), these veins were found to be particularly abundant immediately surrounding the felsic-intermediate intrusions. Type 5 veins are abundant in the A-Porphyry, but less so in the diorites and Teniente Dacite Porphyry, suggesting that they predominantly formed prior to the final emplacement of these units in their respective parts of the deposit. Reflected light analysis of Mo-rich type 5 veins revealed that molybdenite is locally present as large, bladed crystals concentrated at vein margins, associated with quartz (Fig. 9D). In contrast, Cu-rich examples typically exhibit large chalcopyrite crystals intergrown with anhydrite in sites that appear to represent the final stages of vein infill. Mo and Cu grades display no clear relationship with the abundance of type 5 veins in each drill core interval (Fig. 12). This, combined with the fact that type 5 veins account for <6% of veins recorded (Fig. 10), indicates that they are of limited importance in controlling grade distributions in transects 1 to 4.

Quartz-dominated type 6 veins account for ~40% of all veins recorded (Fig. 10) and are observed throughout the Teniente Mafic Complex and within all intrusions (Table 4). These veins display similar abundances at all mine levels (e.g., Fig. 10), but the proportion of Mo-rich type 6a veins generally increases with depth. Mo grades exhibit a stronger positive relationship with type 6a veins than with the abundances of any other vein type in transects 1 and 2 (Fig. 13A, B). This relationship is particularly strong at deep mine levels in the drill cores that intersected the Northern and North-Central

![Fig. 10](image-url)
diorites (DDH 2371 = Transect 1-east; DDH 2215 = Transect 2-east). These drill cores contain fewer type 6a veins than the drill cores that traversed the Teniente Mafic Complex to the west, suggesting that Mo-poor type 6a veins also formed in more distal settings of the Teniente Mafic Complex relative to the diorites. However, Mo grades in the Teniente Mafic Complex still show a stronger relationship with type 6a vein abundance than any other main mineralization vein type. This relationship is also apparent in transects 3 and 4 if the cluster of data with unusually high Mo grades is excluded (Fig. 13B). These high grades are likely to be associated with paragenetically later Mo-rich vein and breccia types that occur at shallow mine levels (Table 3A).

Copper grades display a weak negative correlation with the abundance of type 6a veins (Fig. 14A, B) but show a clear positive correlation with the abundance of type 6b veins (Fig. 14C, D). These chalcopyrite-rich veins are particularly abundant in the Teniente Mafic Complex in the deeper transects (DDH 2363 = T1-west and DDH 2230 = T2-west), where their frequency often exceeds eight veins/meter (Fig. 14C). Three Mo-rich, type 6b vein subtypes that showed clear evidence of early molybdenite mineralization at the vein edges (e.g., Fig.

**Fig. 11.** (A, B) Total number of type 3 veins versus average Mo and Cu grades for 6-m intervals in the two deepest transects (transect 1 = black, transect 2 = gray). (C, D) Abundance of type 3 veins versus average Mo and Cu grades for 20-ft intervals in the two shallowest transects (transect 3 = gray diamonds, transect 4 = black diamonds). Grade data courtesy of Codelco Division El Teniente. TMC = Teniente Mafic Complex.

**Fig. 12.** Total number of type 5 veins versus average Mo (A) and Cu (B) grades for 6-m intervals in the two deepest transects (transect 1 = black crosses, transect 2 = gray crosses) and in the two shallowest transects (transect 3 = gray diamonds, transect 4 = black diamonds). Grade data courtesy of Codelco Division El Teniente.
Fig. 13. (A-H) Total number of main mineralization-stage (type 6a to 8) veins versus average Mo grades (wt %) for 6-m intervals in transects 1 and 2 and 20-ft intervals in transects 3 and 4. Transect 1 (2,250 masl) and transect 2 (1,987 masl) data are plotted on the left-hand column. Transect 1-west = black triangles, transect 1-east = black crosses, transect 2-west = gray triangles, transect 2-east = gray crosses. Transect 3 (gray diamonds) and transect 4 (black diamonds) are plotted on the right. Due to their lack of contained molybdenite, type 7b veins were not plotted. Type 6a veins show the strongest positive correlation with Mo grades of any vein type in all transects. Note the similar trends for drill cores that cut through the Northern Diorite and North-Central Diorite (transect 1-east and transect 2-east), and the similar trends for drill cores that predominantly cut the Teniente Mafic Complex (TMC) host rock to the west of the diorites (transect 1-west and transect 2-west). Brecciated drill core intervals and drill core intervals with >eight late mineralization-stage veins are not plotted. Grade data courtesy of CODELCO Division El Teniente.
Fig. 14. (A-H) Total number of main mineralization-stage (type 6a to 8) veins versus average Cu grades (wt %) for 6-m intervals in transects 1 and 2 and 20-ft intervals in transects 3 and 4. Transect 1 (2,250 masl) and transect 2 (1,987 masl) data are plotted on the left-hand column. Transect 1-west = black triangles, transect 1-east = black crosses, transect 2-west = gray triangles, transect 2-east = gray crosses. Transect 3 (gray diamonds) and transect 4 (black diamonds) are plotted on the right. Due to their lack of contained chalcopyrite and/or bornite, type 7a veins were not plotted. Brecciated drill core intervals and drill core intervals with >eight late mineralization-stage veins are not plotted. Grade data courtesy of CODELCO Division El Teniente.
DISTRIBUTION AND TIMING OF MOLYBDENITE MINERALIZATION AT EL TENIENTE, CHILE

9F-G) or at the vein center with a chalcopyrite overprint (e.g., Fig. 9E) are recognized in this study. Although these Mo-rich examples are relatively abundant within and surrounding all intrusions, type 6b vein abundance displays an inverse correlation with Mo grades in the two deepest transects (Fig. 13B). This trend is similar to the inverse relationship displayed between Cu grades and type 6a vein abundances (Fig. 14A).

Type 7a veins appear to be transitional veins from the quartz-rich type 6a and 6b veins (e.g., Fig. 9I). However, the classification scheme of Vry et al. (2010) does not present a threshold sulfide abundance for this transition. We therefore define type 7 vein as containing >70% sulfides that have no significant associated sericitic alteration. Molybdenite-dominated type 7a veins account for <5% of all veins recorded (Fig. 10) and are typically thin (<2 mm) and commonly discontinuous. These predominantly occur within or proximal to (<20 m) the felsic-intermediate intrusions, in part accounting for the high vein densities and Mo grades surrounding them. However, these veins display no clear relationship with Mo grade (Fig. 13E, F), suggesting that they are of insufficient size and frequency to significantly control Mo grade distribution. Reflected light analysis of several type 7a veins revealed that they do not contain coprecipitated Cu, but are commonly surrounded by significant amounts of disseminated chalcopyrite in the wall rock (e.g., Fig. 9I).

Chalcopyrite-dominated type 7b veins with widths >1 mm are approximately four times more abundant than type 7a molybdenite veins (Fig. 10) and occur throughout the Teniente Mafic Complex, where they have average thicknesses of 5 to 10 mm (Table 4). Despite this, plots of Cu grade against type 7b abundances also display no clear correlations (Fig. 14E, F). This is largely attributed to the fact that, unlike other vein types, type 7b veins are commonly <1 mm thick and, therefore, a considerable proportion (20–40%) were not recorded. This undersampling is particularly likely in the deeper transects and within the felsic-intermediate intrusions where the number of recorded type 7b veins was typically less than five veins/meter, even though chalcopyrite commonly coats fractured drill core surfaces. This is therefore the most problematic limitation of the vein distribution analysis technique used.

Type 8 veins account for approximately 20% of the total number of veins recorded. These veins are particularly abundant at shallow mine levels (e.g., Fig. 10) as well as within drill cores containing abundant Teniente Mafic Complex intervals (Fig. 13G: DDH 2363 = Transect 1-west and DDH 2230 = Transect 2-west). Similar to type 6b veins, type 8 vein abundance generally increases with distance from the felsic-intermediate intrusions (e.g., Fig. 15). These veins are typically composed of more anhydrite and less quartz than the type 6 veins and commonly host significant chalcopyrite, bornite, and pyrite (e.g., Fig. 9K). Molybdenite-bearing type 8 veins are relatively rare (e.g., Fig. 9J), are typically more quartz rich, and generally have narrow alteration halos in which unaltered feldspar can be observed. In rare cases where Mo-rich veins are surrounded by more intense sericitic alteration, reflected light microscopy revealed that molybdenite is typically

### Transect 2: DDH 2215

![Graph](image-url)

**Fig. 15.** Mo and Cu grades (wt %) versus lithology and the abundances of type 6a, 6b, and 8 veins along transect 2 heading to the east of the North-Central Diorite (DDH 2215). Results show fluctuating Mo grades that correlate well with intervals containing abundant type 6a veins. There is a slight decrease in the abundance of type 6a veins and a general increase in type 6b and 8 vein abundances with distance from the intrusion. High Cu grades correlate well with peaks in type 6b and 8 vein abundances (e.g., 136 and 165 m). Decoupling of Mo and Cu is most prominent within 40 m of the intrusion. Abbreviations: DIO = Diorite (North-Central Diorite), TMC = Teniente Mafic Complex.
overprinted by chalcopyrite and/or bornite (e.g., Fig. 9K). This suggests that Mo was deposited prior to a copper sulfide + anhydrite-sericite overprint. Consistent with petrographic observations, Mo grades show no relationship with type 8 vein abundances (Fig. 13G, H). In contrast, type 8 veins display the clearest positive relationship with Cu grade of any vein type in all transects (Fig. 14G, H). Peak Cu grades commonly coincide with peak type 8 vein abundance between 60 and 120 m from the diorite intrusion margins (e.g., Fig. 15).

**Late mineralization-stage veins**

Type 9 tourmaline veins were observed throughout the deposit, cutting all intrusions. These accounted for <1% of veins recorded in transects 1 to 3 (Fig. 10), but for a quarter of veins in transect 4 (Fig. 10). Here they form an apparent vein halo surrounding the Braden Breccia Pipe, in which veins commonly contain abundant molybdenite that is intergrown with or overprints large, acicular tourmaline crystals (e.g., Fig. 9L). Consistent with this, type 9 vein abundance appears to exert a strong control on Mo grades in transect 4, but displays no relationship in transect 3 (Fig. 16A). In contrast, Cu grades tend to be low and consistent (0.6–1.2 wt %) in transect 4 (Fig. 16B) but are generally slightly higher in transect 3 (Fig. 16B), where several chalcopyrite-bearing type 9 veins were observed.

Type 10 anhydrite-carbonate ± gypsum veins were observed crosscutting type 9 veins (e.g., Fig. 9M) and appear to show a close spatial association with concentric and NW-trending faults surrounding the Braden Breccia Pipe (Table 4). Molybdenite is again abundant in these veins and typically occurs at the vein edges alongside variable amounts of bornite ± chalcopyrite. Thin section analysis of a number of these veins revealed clear evidence of reopening, with gypsum, anhydrite, and carbonate overprinting sulfide mineralization (e.g., Fig 10N). Isolated and tarnished fragments of bornite were also observed in several coarse gypsum veins. Although type 10 veins account for <4% of total veins recorded, their abundance displays a strong positive relationship with Mo grade in drill core intervals in the shallow transects (Fig. 16C). In contrast, Cu grades display a highly variable relationship with the abundance of type 10 veins (Fig. 16D) as well as their associated anhydrite-carbonate ± gypsum breccias (e.g., Table 3). This probably reflects the highly variable amounts of contained chalcopyrite and bornite in this stage.

**Breccia-Vein Relationships**

Plots of vein abundance data against lithology for transects 1 to 4 reveal clear spatial relationships between the type 5, 9, and 10 veins and anhydrite-, tourmaline-, and...
anhydrite-carbonate ± gypsum-cemented breccias, respectively. For example, type 5 veins in transect 2 clearly represent vein halos around anhydrite-cemented breccia bodies (Fig. 17). Strong spatial correlations are also observed between type 9 veins and tourmaline breccias in transect 4 (Fig. 18) and between type 10 veins and anhydrite-carbonate ± gypsum breccias in transects 2 (Fig. 17) and 3 (Fig. 19). These breccias and their interpreted vein halos often spatially correlate with elevated Mo and Cu grades. This is particularly noteworthy for Mo, which is generally found at higher levels in sections of drill core that contain tourmaline- (type 9) and anhydrite-carbonate ± gypsum-cemented (type 10) breccias (Figs. 16–18).

**Geochronology**

The timing of mineralization

The 11 molybdenite samples dated in this study by Re-Os document 0.83 million years of mineralization between 5.411 ± 0.022 and 4.584 ± 0.022 Ma (4.580 ± 0.019 Ma replicate: Table 5). This age range is shorter than the 1.9-m.y. range presented by previous studies (Cannell, 2004; Maksaev et al., 2004), which include older Re-Os ages of 6.31 ± 0.03 Ma and 5.60 ± 0.02 Ma (Maksaev et al., 2004), and 5.897 ± 0.020 Ma (Cannell, 2004) for anhydrite breccias associated with the older Sewell Quartz Diorite and A-Porphyry intrusions.

The oldest molybdenite ages recorded in this study are for main mineralization-stage veins within the Southern Diorite and to the north of the Central Diorite (Table 5; Fig. 20). These type 6a, 6b, and 8 veins cluster at ages between 5.411 ± 0.022 and 5.322 ± 0.022 Ma. Molybdenite hosted by the B-fault yields an age of 4.967 ± 0.039 Ma, which coincides with the oldest main mineralization-stage veins spatially associated with the Teniente Dacite Porphyry and Northern Diorite (Fig. 20). Previously dated main mineralization-stage veins in this part of the deposit cluster between 4.980 ± 0.035 and 4.78 ± 0.03 Ma (Fig. 20), correlating well with the type 6b vein from the southern tip of the Teniente Dacite Porphyry dated in this study (4.718 ± 0.023 Ma). These dates also coincide with a molybdenite age of 4.835 ± 0.016 Ma from an anhydrite breccia to the north of the Braden Pipe (Cannell, 2004). Although reported as a late mineralization-stage breccia (Fig. 2), we suggest that this sample may actually represent a type 5 breccia associated with the Teniente Dacite Porphyry that has been overprinted by sericite alteration. These dates also coincide with a transitional type 7a–8 vein and a previously dated type 7a vein proximal to the North Central Diorite (Maksaev et al., 2004), which yielded ages of 4.804 ± 0.020 and 4.83 ± 0.03 Ma, respectively (Fig. 20). These veins are, however, significantly older than a deep-level (1,462 masl), type 6a vein also from the margin of the North Central Diorite that yielded an age of 4.613 ± 0.020 Ma in this study.

Tourmaline breccias on opposite sides of the Braden Pipe yield similar ages of 4.599 ± 0.029 and 4.584 ± 0.020 Ma (Fig. 20). These dates are slightly younger than those of the type 10 vein samples from the western edge of the Central Diorite (1754-373.8) and Southern Diorite (2083-201.2), which yield similar ages of 4.613 ± 0.020 and 4.698 ± 0.023 Ma (4.666...
Fig. 18. Mo and Cu grades (wt %) plotted against host lithology and the abundances of type 9 veins for 20-ft intervals along transect 4 (DDH 1888). Results show a good spatial relationship between the presence of tourmaline breccias (gray columns) and the abundance of type 9 tourmaline veins. These correlate well with peak Mo grades whereas Cu shows no clear relationship with this vein/breccia stage. TMC = Teniente Mafic Complex.

Fig. 19. Mo and Cu grades (wt %) plotted against host lithology and the abundance of type 10 veins for 20-ft intervals along transect 3 (DDH 2083). Peak Mo grades are well correlated with the presence of type 10 anhydrite-carbonate ± gypsum breccias (gray columns), whereas Cu grades show a strong spatial correlation with anhydrite breccias proximal to the Southern Diorite. Mo grades show a spatial association with peaks in the abundance of type 10 veins whereas Cu shows no clear relationship. DIO = Diorite; TMC = Teniente Mafic Complex.
Table 5. Summary of Re-Os Data for the 11 Molybdenite Samples Dated During This Study

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Vein type</th>
<th>Aliquot</th>
<th>Total Vein weight (mg)</th>
<th>t^187Re (ppm) ± 2s</th>
<th>t^187Os (ppb) ± 2s</th>
<th>Common age ± 2s (Ma)</th>
<th>Model age ± 2s (Ma)</th>
<th>Sample description</th>
</tr>
</thead>
</table>
| 2083-229.0 | 6a        | 2,229.9  | 1.35                  | 307.2 ± 3          | 153.2 ± 4         | 8.30 ± 0.2         | 1.1 ± 0.1         | 1-cm-wide type 6a vein containing abundant molybdenite. 
| 1034-587.0 (SEM) | 6a | 1,622.4  | 1.05                  | 107.0 ± 2          | 53.0 ± 0.1        | 8.40 ± 0.1         | 1.1 ± 0.1         | 1-cm-wide type 6a vein containing abundant molybdenite. 
| 1888-133.8 | 8         | 2,277.8  | 1.34                  | 500.5 ± 5          | 0.20 ± 0.01       | 28.36 ± 0.2        | 1.2 ± 0.1         | 1-cm-wide type 8 vein containing abundant molybdenite. 
| 2083-184.1 | 10        | 2,220.6  | 0.98                  | 9.74 ± 0.02        | 0.36 ± 0.01       | 2.42 ± 0.02        | 2.5 ± 0.1         | 1-cm-wide type 10 vein containing abundant molybdenite. 
| 1754-373.8 | 10        | 2,283.1  | 1.37                  | 176.3 ± 0.4        | 0.46 ± 0.01       | 10.91 ± 0.2        | 0.7 ± 0.1         | 2-cm-wide type 10 vein containing abundant molybdenite. 
| 1754-285.9 | 9         | 2,334.4  | 0.92                  | 10.6 ± 0.02        | 0.52 ± 0.01       | 2.42 ± 0.02        | 2.5 ± 0.1         | 1-cm-wide type 9 vein containing abundant molybdenite. 
| 2083-201.2 | 10        | 2,221.2  | 0.98                  | 4.92 ± 0.02        | 0.24 ± 0.01       | 2.42 ± 0.02        | 2.5 ± 0.1         | 1-cm-wide type 10 vein containing abundant molybdenite. 
| 1754-357.8 | 10        | 2,271.2  | 0.98                  | 176.3 ± 0.4        | 0.46 ± 0.01       | 8.51 ± 0.2         | 0.7 ± 0.1         | 2-cm-wide type 10 vein containing abundant molybdenite. 
| B-fault    | None      | 2,210.1  | 1.35                  | 10.6 ± 0.02        | 0.52 ± 0.01       | 2.42 ± 0.02        | 2.5 ± 0.1         | 1-cm-wide type 10 vein containing abundant molybdenite. 

Notes: Replicate (gray) cells = complete new analysis of existing mineral separate; SEM = Os analysis completed using a secondary electron multiplier (weak signal); in these cases the replicate sample ages were the most accurate. Elev. = elevation of sample in meters above sea level; TMC = Teniente Mafic Complex; see Figure 5 caption for abbreviations.
± 0.023 Ma replicate). These ages are similar to a previously dated, late mineralization-stage breccia associated with the latite dike to the southwest of the Braden Pipe (Fig. 20; Cannell, 2004). The youngest Re-Os molybdenite dates at El Teniente are from three unusually young type 8 veins proximal to and within the Teniente Dacite Porphyry and Northern Diorite (Fig. 19) dated by Maksaev et al. (2004; see Fig. 20).

Sample Re contents and validity

Re contents are relatively high and consistent for all the main mineralization-stage samples (171.8–500.5 ppm) with the exception of the type 8 vein sample, which contains highly elevated Re (1,203.6–1,228.4 ppm). This vein type also accounted for the highest Re concentrations recorded in the two previous Re-Os dating studies, where Re concentrations of up to 829.7 ppm were recorded (Cannell, 2004; Maksaev et al., 2004). In contrast, Re concentrations in molybdenite in the late mineralization-stage veins and breccias and in the B-fault are consistently lower (13.71–176.3 ppm).

Stein et al. (2001) stated that variations in the Re contents of molybdenite are most likely to be explained by a simple mass balance phenomenon (Stein et al., 2001): as Re is highly compatible in molybdenite, it will be effectively incorporated into the molybdenite crystal structure in preference to other sulfide species (Stein et al., 2001). Therefore, if only minor amounts of molybdenite and abundant copper sulfides are precipitated, the molybdenite will contain higher Re concentrations. This explains the elevated Re concentrations in molybdenite-bearing type 8 veins which, in accordance with petrographic observations and vein distribution data, are commonly associated with abundant chalcopyrite ± bornite and only minor Mo mineralization.

In contrast to type 8 veins, mineralization in the B-fault and in the late mineralization stage veins and breccias is dominated by molybdenite and only minor quantities of Cu sulfides. This means that low Re concentrations are likely to be a manifestation of Re dilution during abundant molybdenite crystallization. This is consistent with a comparison study of Re in molybdenite from the Endako porphyry Mo deposit and the Nithi Mountain occurrence, British Columbia, where lower Re concentrations at Endako were attributed to the far greater extent of Mo mineralization (Selby and Creaser, 2001). Similar observations have also been made in the Qinling belt, China (Stein et al., 1997), and in comparison studies between porphyry Cu-Mo and Mo deposits (Giles and Schilling, 1972), both of which showed decreasing Re concentrations in molybdenite deposited during Mo-rich stages.

Suzuki et al. (2000) suggested that the Re-Os molybdenite system may be disturbed in the presence of hot, low-salinity fluids (<1 wt % NaCl equiv). However, a recent study by
Selby and Creaser (2001) concluded that the Re-Os system is undisturbed by low to moderately saline (1–15 wt % NaCl equiv) hydrothermal fluids. Previous fluid inclusion microthermometric studies at El Teniente (Cannell, 2004; Klemm et al., 2007; Vry, 2010) revealed that, with the exception of rare, low-density, vapor-like inclusions, the majority of fluid inclusions at El Teniente have salinities > 1 wt % NaCl equiv. Therefore, the samples dated in this study are unlikely to have been affected by hydrothermal overprinting. This, combined with the young age of El Teniente and the fact that the Re-Os molybdenite system shows closed-system behavior during ductile deformation and regional metamorphism (e.g., Stein et al., 1998; Selby and Creaser, 2001; Lawley and Selby, 2012), suggests that the dates obtained during this study represent true mineralization ages.

The three replicate samples yielded ages that agree within calculated uncertainty limits (Table 5), taking into account all procedural uncertainties. The reproducibility of these sample ages suggests that the technique used was effective in producing accurate age determinations and that no samples were analyzed that contained mixed generations of molybdenite. With the exception of two samples, all calculated uncertainties are ≤ 0.023 m.y. (Table 5). However, one type 10 vein sample (2083-201.2) and the B-fault sample have higher analytical uncertainties, mainly due to their low Re concentrations (Table 5). The replicate run for the type 10 vein sample yielded a lower degree of uncertainty, which was achieved by running a larger aliquot weight of molybdenite. Low Re concentrations are also documented for molybdenite in the tourmaline breccia samples from opposite sides of the Braden Breccia Pipe. However, these samples yielded Re-Os ages that are within calculated uncertainties of one another as well as the tourmaline breccia replicate, thus suggesting that the technique used was effective in producing reproducible age determinations for molybdenite samples that contain very low Re concentrations.

Discussion

Geochronological constraints on the evolution of El Teniente

Mineralized vein and breccia distributions provide strong evidence that the A-Porphyry, diorites, and Teniente Dacite Porphyry all played integral roles in controlling deposit-wide grade distributions as previously proposed (e.g., Cannell et al., 2005; Vry et al., 2010). The large ranges of U-Pb zircon crystallization ages recorded for these intrusions (Fig. 3: Maksae et al., 2004) are interpreted to reflect age determinations made on zircon antecrysts that crystallized over an extended period of time in the underlying parental magma chamber and occasional younger ages due to zircon overgrowths or post-crystallization lead loss. We therefore infer that the youngest distributions of reliably dated, overlapping zircon ages (1σ) provide the best constraints for the timing of emplacement and final crystallization of each intrusion (cf. von Quadt et al., 2011).

Based on our reinterpretation of U-Pb zircon data, we agree with Maksae et al. (2004) that the crystallization of the A-Porphyry is likely to have occurred between 6.0 and 5.7 Ma, following the emplacement of the Sewell Quartz Diorite. In contrast, we suggest that crystallization of the Central and Northern diorites is likely to have occurred between 5.6 and 5.3 Ma (Fig. 21). This window correlates with the subordinate peak in U-Pb zircon ages recorded for these intrusions (Maksae et al., 2004) and explains the presence of molybdenite Re-Os ages of 5.411 ± 0.022 to 5.322 ± 0.022 Ma for main mineralization-type veins within and proximal to them. Based on petrological evidence and the spread of U-Pb zircon and Re-Os molybdenite ages associated with the Teniente Dacite Porphyry, we interpret a prolonged crystallization history for this unit occurring in multiple intrusion-mineralization pulses between 5.1 and 4.7 Ma (Fig. 21). This age range is younger than the weighted average 206Pb/238U age of 5.28 ± 0.10 Ma reported by Maksae et al. (2004), which possibly incorporates older zircon antecrysts. A younger crystallization age between 4.6 and 4.4 Ma is also inferred for the late dacite dike encircling the Braden Pipe. The late formation of such dikes may explain the younger Re-Os ages of type 8 veins in the northern part of the deposit dated at 4.42 ± 0.02 Ma (Maksae et al., 2004). Based on the overall younging of U-Pb dates from the Sewell Quartz Diorite and the A-Porphyry in the south to the Northern Diorite and the Teniente Dacite Porphyry in the north, we infer a general northward progression of the locus of magmatism over the ~1.6-m.y. total lifetime of the mineralizing system.

The apparent correspondence between intrusion crystallization ages and Re-Os ages determined in this and the two previous studies (Maksae et al., 2004; Cannell et al., 2005) strongly supports the field evidence that mineralization occurred in pulses during and after the emplacement of each of the main intrusions—the A-Porphyry, diorites, and during several stages of emplacement and crystallization of the Teniente Dacite Porphyry (Fig. 21; Vry et al., 2010). The relative rarity of the reverse crosscutting vein and breccia relationships that might be expected in a system involving repeated mineralization cycles can be explained by the northward progression of magmatism (so that successive porphyries did not intrude each other), combined with the vertically elongate aspect ratios of the mineralized centers (limiting lateral overprinting of one center by another).

The deposit-wide vein paragenesis and associated fluid evolution espoused in several previous studies (e.g., Cannell et al., 2005; Klemm et al., 2007) is disproved by our new Re-Os ages. For example, a type 6a-7a transitional vein between the Central Diorite and North Central Diorite has a relatively old age of 5.322 ± 0.022 Ma, consistent with the inferred emplacement age range of the Central and Northern diorites, whereas a deep type 6a vein from within the North-Central Diorite has a significantly younger age of 4.613 ± 0.020 Ma (Table 5, Fig. 20). Some type 8 veins formed as early as 5.375 ± 0.022 Ma (proximal to the Southern Diorite), clearly before a number of type 6 and 7 veins from the northern part of the deposit dated in this and previous studies (e.g., 4.805 ± 0.016 Ma; Cannell, 2004). Early type 8 vein development in the southern part of the system refutes the argument that there was a deposit-wide transition into sericite-stable conditions (type 8 vein stage) at ~4.95 Ma (Cannell, 2004). Sericite alteration is the result of the dissociation of acids and the disproportionation of magmatic sulfur dioxide (e.g., Giggenbach, 1992; Rye, 1993; Heinrich et al., 2004) in response to drops in temperature and pressure (Meyer and Hemley, 1967; Reed and
Fig. 21. (A) Time versus depth plot showing the magmatic-hydrothermal evolution of El Teniente based on field observations and geochronology. Intrusion and breccia colors match geologic map (Figs. 2, 6). The positions of Mo and Cu mineralization relate to enriched ore zones (>0.03% Mo, >1.5% Cu) surrounding each intrusion and are based on grade distributions, vein crosscutting relationships, and Re-Os dates collected during this and the two previous studies (Cannell, 2004; Maksaev et al., 2004). The inferred paleosurface is a conservative estimate (max. 5,300 masl at 5 Ma). Dotted green line = deepest drillcore depth studied, below which significant Mo grades are interpreted to extend. (B) Re-Os dates from this study (blue circles) and the two previous studies (green and red circles; see key). The five mineralizing pulses proposed by Maksaev et al. (2004) are shown in gray columns. Dotted boxes represent the youngest reliable overlapping U-Pb zircon dates previously obtained for each intrusion (Maksaev et al., 2004).
The consistent breccia and vein parageneses for the main stage of mineralization associated with each intrusion (Vry et al., 2010) are indicative of a relatively stable and fertile underlying magma chamber that fueled geochemically similar pulses of mafic-intermediate magmatic-hydrothermal fluids through each porphyry intrusion. The vein distribution analysis reveals that each intrusion developed similar vein halos, consisting of vein types that exhibit relatively uniform abundances and spatial configurations in each mineralized center. Combining Re-Os and U-Pb zircon ages, we interpret at least three major magmatic pulses, each separated by approximately 0.3 m.y. (Fig. 21). These pulses may consist of several emplacement events (as in the case of the composite Teniente Dacite Porphyry), with up to nine distinct mineralization cycles identified (Fig. 21). This interpretation is consistent with paleomagnetic data from the deposit that document complex polarity zonation, suggestive of numerous pulses of hydrothermal activity (Astuillo et al., 2010).

Molybdenite Re-Os dates from within and surrounding the Southern Diorite suggest that main mineralization-type veins associated with this intrusion formed over a relatively short timescale, within about 100,000 years (Table 5; Fig. 21). This age range is consistent with an ~50,000-year time gap between U-Pb zircon ages (closure temperature ~1,000°C) and 40Ar/39Ar ages for hydrothermal biotite (closure temperature ~300°C) previously recorded for a mineralized dacitic dike at El Teniente (Maksaev et al., 2004). These age ranges are also in accordance with previous studies which concluded that the emplacement of an intrusion and the subsequent focusing of large fluid fluxes through it are likely to occur on a time scale of 10,000 to 100,000 years (Cathles, 1977; Driesner and Geiger, 2007; von Quadt et al., 2011). Relatively rapid heat loss in this environment can be attributed to significant heat advection by magmatic fluids and can explain the inward and downward overprinting of late, chloropyrite-rich type 6b and 7b veins over molybdenite-rich type 6a and 7a veins. Thermal contraction during each mineralization cycle may also explain the overprinting of high-temperature veins by sericite-altered type 8 veins. Although type 8 veins are most abundant in distal parts of the Teniente Mafic Complex relative to the felsic-intermediate intrusions, examples were also observed overprinting type 6a veins within the mineralized intrusions and occurring at the greatest depths currently accessible.

Molybdenite Re-Os dates within and proximal to the Southern and Central diorite clusters between 5.4 and 5.3 Ma and correlate well with crystallization ages for the Central Diorite (Maksaev et al., 2004). Unfortunately, no emplacement ages currently exist for the Southern Diorite. Significantly younger molybdenite ages of ~4.8 to 4.6 Ma were obtained for main mineralization-type veins within and proximal to the North-Central Diorite and Northern Diorite (Fig. 20). Based on these results, it is possible that these northern diorites were emplaced approximately synchronously with the Teniente Dacite Porphyry and mineralized approximately 0.6 m.y. later than the diorites farther south. However, this is contradicted by relatively old zircon ages obtained from the Northern Diorite, which fall between 5.3 and 6.7 Ma. To date, no crystallization ages have been obtained for the North-Central Diorite. Given this, it is currently not possible to say whether the Northern Diorite and North-Central Diorite developed later. In addition, it is unclear whether zircons dated in the Northern Diorite reflect final crystallization, or whether we sampled veins associated with older intrusions that were reactivated as hydrothermal fluid conduits during pulses of magmatism and mineralization accompanying emplacement of the Teniente Dacite Porphyry.

Mineralization within the B-fault occurred at approximately 5.0 Ma and corresponds with the oldest Re-Os dates obtained for main mineralization-type veins associated with the Teniente Dacite Porphyry (Fig. 20). This suggests that the N-trending faults may have developed synchronously with the emplacement of this intrusion (Fig. 21). Evidence for right-lateral, strike-slip displacement is observed along several NW-trending faults at El Teniente, including the B-fault. An E-W-oriented minimum principal stress is consistent with dextral strike-slip motion on these faults and the opening of the N-S fractures that accommodated emplacement of the Teniente Dacite Porphyry dike and, possibly, the North-Central Diorite and Northern Diorite. Thus, initiation of movement along the B-fault and related structures is interpreted to have been the trigger that rejuvenated shallow magmatism and hydrothermal activity following a hiatus of ~300,000 years (Fig. 21). The orientation of the diorite intrusions along a similar northerly trend to the Teniente Dacite Porphyry suggests that a similar tectonic trigger could have been responsible for the earlier major pulses of magmatism.

Main mineralization-type veins dated along the Teniente Dacite Porphyry dike predominantly fall between 5.00 and 4.42 Ma (Fig. 20). This extended (~580,000-year) period of mineralization is attributed to the fact that the Teniente Dacite Porphyry formed as a composite intrusion composed of several overlapping dikes (Fig. 21), as constrained by petrological observations, geochemical studies, and previous geochronology that documents up to 1 m.y. of magmatism along the dike (Ossandón, 1974; Duarte, 2000; Skewes et al., 2002; Rojas, 2003; Maksaev et al., 2004; Cannell et al., 2005; Hitschfeld, 2006; Baker et al., 2013). The three, unusually young, type 8 veins proximal to the Teniente Dacite Porphyry and Northern Diorite (4.42 Ma: Maksaev et al., 2004) post-date all U-Pb zircon ages for the Teniente Dacite Porphyry by 0.3 m.y. (Fig. 3), but do coincide with the youngest 40Ar/39Ar sericite ages recorded in this part of the deposit. Given this, we concur with Maksaev et al. (2004) that these veins represent minor, late pulses of hydrothermal activity related to the emplacement of small dacitic dikes during the waning of the magmatic system (Fig. 21).

The close spatial association of Mo-rich type 9 to 10 veins and breccias with the margin of the Braden Breccia Pipe suggests that the late mineralization stage is closely linked to this cataclastic event. Concentric faults and fractures surrounding the Braden Breccia Pipe (Fig. 2) are interpreted to be the result of a period of subsidence related to magma withdrawal prior to the Braden Breccia event (Koide and Bhattacharji, 1975; Acocella et al., 2000; Cannell et al., 2005). The close
spatial association of these faults with the well-defined Mo-rich halo around the Braden Breccia observed at shallow mine levels (Fig. 20) suggests that they were important in focusing late, Mo-mineralizing fluids into the upper parts of the deposit to form type 9 and 10 veins. This occurred over a relatively short time period between 4.698 ± 0.040 and 4.584 ± 0.020 Ma (Fig. 20; Table 5).

The formation of type 9 and 10 veins is likely to have been immediately followed by a major release of magmatic volatiles that formed the Braden Breccia Pipe (e.g., Cannell et al., 2005). This major brecciation event cut the Mo-rich tourmaline breccias, leading to the formation of a large rock-flour breccia diatreme with an apparent Mo-rich marginal facies. This evolution is supported by the absence of crosscutting type 9 veins in the Braden Breccia and the presence of considerable amounts of brecciated type 9-related tourmaline within the diatreme margins. Type 10 veins are also absent in the Braden Breccia. However, cavities and fractures within the diatreme do contain considerable amounts of coarse-grained gypsum, possibly generated by the ingress of circulating groundwater into the breccia pipe. U-Pb zircon ages for a ring dike linked to the formation of the Braden Breccia Pipe (Maksaev et al., 2004) and K-Ar sericite dates from within and surrounding the breccia diatreme (Cuadra, 1986) led to the interpretation that this formed between 4.82 and 4.60 Ma. However, the consistent molybdenite ages in the marginal tourmaline breccias on opposing sides of the Braden Breccia Pipe (4.599 ± 0.029 and 4.584 ± 0.020 Ma; Table 5) suggest that it was emplaced at or shortly after 4.6 Ma (Fig. 21).

Controls on decoupling of Mo and Cu mineralization

Based on vein and grade distribution data, we agree with previous studies that approximately 80% of the Cu at El Teniente is hosted within veins and as minor disseminations in the Teniente Mafic Complex (Camus, 1975; Vry et al., 2010), suggesting that this mafic host-rock sequence is an effective physical and chemical trap for copper sulfide deposition. Approximately 10% of the Cu is hosted by breccias (Cannell et al., 2005, 2007) and the remaining 10% Cu occurs within the intrusions that acted as conduits for mineralizing fluids. In contrast, grade distribution data reveal that Mo grades are generally more elevated in the intrusions (e.g., Fig. 22) as well as in the cements of late mineralization-stage breccias (e.g., Figs. 18–20). Based on intrusion and breccia volumes and their enriched Mo grades relative to Cu at different mine levels, we estimate that up to 20% of the Mo is hosted within breccias and approximately 20% is hosted within the intrusions. The remaining 60% is hosted within veins in the Teniente Mafic Complex, predominantly in type 6a veins surrounding each mineralized intrusion, as well as in late mineralization-stage veins that surround the Braden Breccia Pipe at shallow mine levels.

The relative rarity of sulfide-bearing, premineralization-stage veins indicates that only minor mineralization accompanied potassic alteration and biotitization of the Teniente Mafic Complex, as previously proposed (Camus, 1975; Cuadra, 1986; Maksaev et al., 2004; Cannell et al., 2005; Vry et al., 2010). The first paragenetic stage containing elevated Mo and Cu grades relates to the formation of anhydrite breccias (Table 3A-B) that cap the felsic-intermediate intrusions. Although these breccias may be well mineralized, the poor relationship between the abundance of the type 5 anhydrite breccias in the surrounding vein halos and Cu and Mo grades (Fig. 12) suggests that most sulfides during stage 5 were precipitated proximal to the intrusions and that the ore within the surrounding Teniente Mafic Complex is controlled by later main stage-type veins.

The overlap of Mo and Cu grade halos (e.g., Figs. 7, 8) and the comparable Re-Os dates for Mo- and Cu-rich type 6a to 8 veins surrounding the porphyry intrusions (Fig. 20) suggest that both metals were deposited during the same pulses of magmatic-hydrothermal activity and are not entirely decoupled in time. Vein distribution data indicate that most Mo was precipitated in type 6a veins within and proximal to

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**Fig. 22.** Mo versus Cu grades (wt %) for different lithologies in transects 1 to 4. (A) Grades for 6-m drill core intervals in transects 1 and 2, where intrusions (gray triangles) are the Northern and North-Central diorites. (B) Mo versus Cu grades for 20-ft intervals in transects 3 and 4, where intrusions are the Teniente Dacite Porphyry and the Central and Southern diorites. Mo/Cu ratios are generally high in the intrusions and low in the Teniente Mafic Complex (TMC).
the intrusions (Fig. 13A), whereas Cu is principally hosted by outboard type 6b, 7b, and 8 veins. The general increase in the abundance of these Cu-rich vein types with distance from the felsic-intermediate intrusions, coupled with a comparable decrease in the abundance of type 6a veins (e.g., Fig. 13), can be interpreted in terms of an outward/upward transition from type 6a veins into type 6b and then type 7 and/or type 8 veins (Fig. 23). This considered, we suggest that main mineralization-stage Mo and Cu were predominantly transported by the same fluids and were sequentially deposited, leading to their decoupled mineralization shells surrounding the intrusions.

The development of Cu-rich veins from Mo-rich type 6a veins is supported by previous fluid inclusion laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) studies that document high Mo and Cu concentrations in fluid inclusions within type 6a veins, whereas fluid inclusions in type 6b and 8 veins typically remain Cu rich but are Mo depleted (Klemm et al., 2007; Vry, 2010). Cooling and consequent downward telescoping of main mineralization-type veins within each magmatic-hydrothermal cycle (Fig. 21) can explain the overprint of “later” Cu-rich veins over paragenetically “earlier” Mo-rich ones. However, it is likely that several of the main mineralization-stage vein types formed synchronously at different depths and distances from the intrusions. There are several ways in which Mo-rich 6a veins may have evolved spatially into type 6b, 7a, 7b, and 8 veins (Fig. 23). Further fluid inclusion analysis of these vein types at different mine levels and distances from the intrusions is required to assess these potential evolution pathways.

Several factors are likely to have influenced Mo and Cu solubility during the development of type 6a to 8 veins. The general restriction of Mo-rich veins to within and immediately surrounding the porphyry intrusions suggests that Mo was deposited at relatively high temperatures. Previous fluid inclusion analysis of type 6a veins suggests likely deposition temperatures in excess of 380°C (e.g., Vry, 2010). In contrast, the close association of Cu with type 8 veins (e.g., Fig. 14G, H) suggests that it was usually deposited at lower temperatures under which significant sericite alteration occurred. Fluid-wall rock interactions may have also played an important role in the sequential deposition of Mo and Cu. As fluids migrated...
outward through the Teniente Mafic Complex, interaction with reduced iron-bearing silicates is likely to have led to fluid reduction. Previous studies have demonstrated that as log f O₂ decreases below NNO + 1, molybdenite saturation is favored over chalcopyrite (e.g., Andéat and Pettke, 2006; Seo et al., 2012). This could explain the early deposition of Mo in type 6a veins proximal to the intrusion margins and the outboard deposition of chalcopyrite (Fig. 23).

The formation of the relatively rare type 7a molybdenite veins can be explained by upward/outward advective flow down pressure gradients leading to retrograde quartz solubility (e.g., Vry et al., 2010). The fact that the type 7a veins are commonly surrounded by significant disseminated chalcopyrite suggests that they were formed from Cu-bearing fluids, with relatively high temperature and f O₂ conditions inhibiting Cu precipitation proximal to the intrusions. Alternatively, the formation of type 7a veins could be the result of the exsolution of separate pulses of Mo-rich and relatively Cu poor fluids from the magmatic source. Further fluid inclusion analysis is required to test this hypothesis.

The presence of numerous, thick, type 7b veins within the Teniente Mafic Complex suggests that fluid-wall rock interactions played an important role in triggering the precipitation of chalcopyrite (Fig. 23). However, previous fluid inclusion studies also revealed an apparent increase in the abundance of boiling assemblages in Cu-rich type 6b to 8 veins (Cannell, 2004; Klemm et al., 2007; Vry, 2010), so vapor-brine partitioning may also have played a role in Cu deposition, perhaps via loss of sulfur species to the low-density vapor and consequent destabilization of Cu sulfide complexes. The comparative rarity of brine-vapor assemblages reported in Mo-rich type 6a veins suggests that vapor-brine separation was less likely to have been important in controlling Mo deposition.

Type 8 veins display the strongest decoupling between Mo and Cu grades of any main mineralization-type vein (Figs. 14G, H, 15G, H). The rarity of type 8 veins containing molybdenite, as well as the fact that these rare examples commonly contain unalteredfeldspar in their alteration halos, suggests that most Mo was deposited prior to significant acid dissociation, whereas Cu was frequently deposited under cooler and more acidic conditions (Fig. 23). A detailed fluid inclusion LA-ICP-MS study is currently underway to test the proposed vein evolution model and to assess the conditions under which Mo and Cu were deposited as hydrothermal fluids migrated outward from each intrusion.

The abundance of Cu sulfide (especially bornite)-bearing main mineralization-type veins surrounding the Teniente Dacite Porphyry suggests that this intrusion was responsible for much of the shallow-level Cu mineralization in this part of the deposit (Camus, 1975; Maksaev et al., 2004; Cannell et al., 2005; Vry et al., 2010). In contrast, Mo grades in this area are strongly controlled by late mineralization-stage veins and breccias that overprint Cu mineralization and that have been dated at approximately 4.6 Ma (Fig. 20). The relatively Cu poor nature of late mineralization-stage veins and breccias is interpreted to be the result of the earlier extraction of Cu from the underlying magma chamber by previous cycles of release of S-rich magmatic fluids (e.g., Zając and Halter, 2009). This could have created a Cu-poor residual melt that became progressively enriched in incompatible Mo during the final stages of crystallization (e.g., Candela and Holland, 1984; Audéat, 2010).

The late exsolution of Mo-rich fluids from a highly fractionated magma chamber could explain why Mo grades associated with late mineralization-stage veins and breccias are typically two to three times higher than those associated with main mineralization-stage veins. Late pulses of deep-sourced, oxidized, Mo-rich fluids may have exploited recently opened faults to form the concentric and NW-trending configuration of anhydrite-dominated, late mineralization-stage veins and breccias at shallow mine levels. This focusing of Mo into structural traps may explain the unusually high Mo grades of up to 0.35 wt % recorded in some drill core intersections at shallow mine levels. Alternatively, significant amounts of Mo may have been sourced by remobilization, as previously suggested (Vry et al., 2010). Mo remobilization could explain the apparent rarity of Mo-rich main mineralization-stage veins associated with the Teniente Dacite Porphyry, which, according to the proposed model of transitional vein development, should occur below Cu-rich veins in this part of the deposit. In addition, this process may explain why peak Mo grades occur slightly outboard of the Braden Breccia Pipe margin. Although both mechanisms are possible, the physical and chemical characteristics of late mineralization-stage fluids remain poorly constrained. Further fluid inclusion studies are required to identify the origin and reasons for the high Mo contents of these late-stage fluids, which, to date, have not been studied in detail.

Summing up, the combination of geochronological, vein distribution, and grade data suggests that magmatic processes probably do not control the spatial and temporal decoupling of Cu and Mo at El Teniente, although the late, high Mo grades could be attributed to the long-term evolution of Mo:Cu ratios in the underlying magma reservoir. In general, Cu and Mo were probably transported by the same fluids, with their tendency to precipitate in distinct vein types being related to varying temperature, pressure (e.g., Ulrich et al., 2002; Redmond et al., 2004; Landtwing et al., 2005; Ulrich and Mavrogenes, 2008; Rusk et al., 2008), and redox state of fluids (e.g., Phillips et al., 1974; Sillitoe, 2010; Seo et al., 2012) as they exited the porphyry intrusive conduits and migrated out into fractured mafic rocks of the Teniente Mafic Complex.

Conclusions

Combined grade and vein distribution analysis and high-precision Re-Os dating at El Teniente provide valuable insights into the genetic links between different intrusions, breccias, and vein types and enable a quantitative assessment of their importance with respect to economic mineralization. Mo and Cu grades both show a strong spatial-temporal relationship with the A-Porphyry, diorites, and Teniente Dacite Porphyry, which acted as conduits for pulses of magmatic-hydrothermal fluids. These each developed their own, relatively localized, main mineralization-type vein halos that closely followed the same breccia and vein chronology. Re-Os dating provides evidence that there was no single, deposit-wide evolution in vein types and their associated fluids as previously proposed. Results are indicative of the systematic development of relatively localized ore shells surrounding the intrusions, which developed during and immediately after their crystallization. Intrusion-mineralization pulses...
appear to be relatively short-lived (<100,000 years), with more prolonged mineralization surrounding the Teniente Dacite Porphyry attributed to its extended intrusion history. The emplacement of this northward-trending intrusion is likely linked to the development of NW-trending faults that underwent dextral strike-slip displacement at approximately 5.0 Ma. Individual pulses of magmatic-hydrothermal activity are separated by quiescent periods of up to 300,000 years, documented by distinct gaps in the ages of shallow-level molybdenite mineralization.

Vein distribution analysis reveals that type 6a quartz-molybdenite veins are the most important control on deposit-wide Mo grade distributions. The importance of these veins is particularly notable in close proximity to the felsic-intermediate intrusions and at deep mine levels, where their abundance controls typical grades of 0.01 to 0.06 wt % Mo. In contrast, Cu grades of up to 2.4 wt % are principally controlled by the abundances of type 6b, 7b, and 5 veins that occur in more distal positions relative to the porphyry intrusions. These vein types appear to be upward and outward transitional veins from higher-temperature 6a veins, suggesting that sequential deposition of metals as a result of decreasing temperature and fO₂ was the main driving force in Mo-Cu decoupling during each cycle of main mineralization-type veining.

Mo grades >0.06 wt % are controlled by the presence of late mineralization-stage veins and breccias that show a close spatial association with faults and fractures surrounding the Braden Pipe at shallow mine levels. The generally Cu poor nature of this paragenetic stage is attributed to the prior preferential extraction of Cu from the underlying magma chamber in the previous mineralizing events. This led to the development of an Mo-rich residual melt phase that exsolved oxidized, Mo-rich fluids that overprinted Cu mineralization at approximately 4.60 Ma. During this event, remobilization of Mo may have also increased Mo concentrations in late mineralization-stage fluids, explaining the apparent lack of molybdenite-bearing main mineralization-type veins at depth proximal to the Teniente Dacite Porphyry. The late mineralization stage was terminated by the formation of the Braden Breccia Pipe in a single explosive event at approximately 4.58 Ma. With the exception of minor mineralization associated with small dacitic dikes, this event marked the termination of Mo and Cu sulfide deposition at the deposit.

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REFERENCES


