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LETTER

# Timing and duration of hydrothermal activity at the Los Bronces porphyry cluster: an update

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**Abstract** New geochronological data from the Los Bronces cluster of the Río Blanco-Los Bronces mega-porphyry Cu-Mo district establish a wide range of magmatism, hydrothermal alteration, and mineralization ages, both in terms of areal extent and time. The northern El Plomo and southernmost Los Piches exploration areas contain the oldest barren porphyritic intrusions with U-Pb ages of 10.8±0.1 Ma and 13.4±0.1 Ma, respectively. A hypabyssal barren intrusion adjacent northwesterly to the main pit area yields a slightly younger age of 10.2±0.3 Ma (San Manuel sector, U-Pb), whereas in the Los Bronces (LB) open-pit area, the present day mineral extraction zone, porphyries range from 8.49 to 6.02 Ma (U-Pb). Hydrothermal biotite and sericite ages are up to 0.5 Ma younger but consistent with the cooling of the corresponding intrusion events of each area. Two quartz-molybdenite B-type veins from the LB open pit have Re-Os molybdenite ages of 5.65±0.03 Ma and 5.35±0.03 Ma consistent with published data for the contiguous Río Blanco cluster. The San Manuel exploration area within the Los Bronces cluster, located about 1.5–2 km southeast of the open-pit extraction zone, shows both the oldest hydrothermal biotite (7.70±0.07 Ma; $^{40}Ar/^{39}Ar$) and breccia cement molybdenite ages (8.36±0.06 Ma; Re-Os) registered in the entire Río Blanco-Los Bronces district. These are also older than those reported from the El Teniente porphyry Cu(-Mo) deposit, suggesting that mineralization in the late Miocene to early Pliocene porphyry belt of Central Chile commenced 2 Ma before the previously accepted age of 6.3 Ma.

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## Introduction

The Río Blanco-Los Bronces Cu-Mo porphyry district is part of the Miocene-Pliocene metallogenic belt in central Chile (Fig. 1), and is located between latitudes 33°07’45” and 33°10’20” S, 65 km northeast of Santiago at about 3,500–4,500 m a.s.l. The district hosts different interconnected ore bodies which can be described as a mega-porphyry Cu (-Mo) cluster, currently exploited by Andina Division (Codelco) at Rio Blanco and by Anglo American plc at Los Bronces, San Enrique Monolito, and Los Sulfatos. The Río Blanco underground and open-pit mines produce about 250,000 metric tonnes (t) of Cu and 2,500 t of Mo per year. The Los Bronces open-pit mine produces annually 400,000 t of fine copper and 2,000 t of Mo. A recent mineral inventory estimate for the Los

Bronces-Rio Blanco cluster, including areas such as San Enrique Monolito and Los Sulfatos (Anglo American plc.) at the southeastern extreme, reports an inferred total resource of 204 Mt of fine copper (Irarrázaval et al. 2010), positioning the cluster as the largest Cu-Mo porphyry-breccia system in the world.

The entire ore district has been related to one single igneous-hydrothermal mineralization system. Hypogene Cu-Mo mineralization in the Río Blanco cluster probably persisted between 6.3 and 4.4 Ma, for ca. 2 Ma (Deckart et al. 2005, 2013). Toro et al. (2009) presented a slightly wider age range between 7.5 and 4.5 Ma for the entire Rio Blanco-Los Bronces cluster, which is supported by previously published K-Ar and Ar-Ar ages (Serrano et al. 1996).

The aim of this paper is to present first Re-Os geochronological data on molybdenite veins and breccia cement obtained from four areas belonging to the Los Bronces cluster and new U-Pb laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) ages on zircon and $^{40}Ar/^{39}Ar$ ages on hydrothermal biotite and sericite. Furthermore, these new data will be discussed in the context of those of the eastward contiguous Río Blanco cluster (Deckart et al. 2005, 2013) as well as the age constraints from the entire Mio-Pliocene metallogenic belt of Central Chile (Camus 2003).

## Geologic setting of the Río Blanco-Los Bronces porphyry cluster

### Pre- and post-mineralization rock units

The Río Blanco-Los Bronces porphyry Cu-Mo deposits are hosted by the volcaniclastic Farellones Formation (17.2 to 16.7 Ma, U-Pb; Deckart et al. 2005) and the Eocene to earliest Miocene Abanico Formation as well as by the San Francisco batholith (SFB), which intrudes these volcanic units. The overall coarse-grained granodioritic to dioritic SFB temporally and spatially is composed of two distinct magmatic pulses at 14.8 (Munizaga 1994; Deckart et al. 2010) and 11–12 Ma (Waarnars et al. 1985; Deckart et al. 2010). Two fine-grained, locally porphyritic intrusive units of the San Francisco batholith have been recognized in the Río Blanco cluster: the Cascada granodiorite (8.40±0.23 Ma) and the Diorite (8.16 ±0.45 Ma) (U-Pb ID-TIMS zircon dating, Deckart et al. 2005). These are notable younger than other ages of the SFB but considered to be pre-mineralization. Magmatic activity ended with the emplacement of the late- to post-mineralization Dacite Plug event belonging to the La Copa Volcanic Complex (Fig. 2; 4.92±0.09 Ma; Deckart et al. 2005) at the Río Blanco cluster. Between 4.7–4.1 Ma, the hydrothermal activity decreased, associated with the emplacement of the Rhyolite Plug (La Copa Volcanic Complex; Fig. 2) and related extrusion of a suite of explosive breccias and ignimbrite deposits.

### Previously published ages on hydrothermal activity

The three inter- to late-mineral main hypabyssal porphyritic intrusions recognized in the Río Blanco cluster (PQM: quartz-monzonite porphyry, PDL: Don Luis porphyry, FP: feldspar porphyry), associated with the Cu-Mo mineralization, cover an age range from 7.1±0.2 to 5.2±0.1 Ma (U-Pb ID-TIMS and SHRIMP II; Deckart et al. 2005, 2013).

Ages obtained on distinct molybdenite veins of the Río Blanco cluster indicate an age range from 5.94±0.03 to 4.50 ±0.02 Ma (Deckart et al. 2013). When including the molybdenite data of Mathur et al. (2001) of 5.31±0.03 to 6.26± 0.04 Ma, a time span of at least 1.82 Ma for the hydrothermal activity is suggested. The potassic and phyllic hydrothermal alteration overlaps with the molybdenite ages and ranges between 5.89 and 4.24 Ma ($^{40}Ar/^{39}Ar$; Deckart et al. 2005, 2013), the phyllic alteration being the paragenetically youngest event. It is suggested that the late- to post-mineralization La Copa Volcanic Complex has triggered a general thermal resetting of $^{40}Ar/^{39}Ar$ ages in the entire Cu-Mo porphyry cluster. Finally, it is worth noting that at least one early discrete advanced argillic alteration event, apparently sub-economic, has been recognized in the Ortiga-Los Piches area of 8×5 km, about 8 km west of the LB open pit (Fig. 2), mainly in the volcaniclastic Abanico Formation and in and adjacent to the San Francisco batholith (12.3±0.1 Ma, hypogene alunite; Eggers 2009).

Published age constraints for Los Bronces are less complete and more ambiguous than for Rio Blanco. Warnaars et al. (1985), based on twelve K-Ar ages, concluded that the Los Bronces hydrothermal system formed over an interval of 2.5 Ma between 7.4 and 4.9 Ma, a time span that includes breccia formation in the district. Skewes et al. (2002) used biotite $^{40}Ar/^{39}Ar$ data (Skewes 1997) to extend the emplacement interval of mineralized breccias at Los Bronces from 14 to 4 Ma. Toro et al. (2007); Toro et al. 2012) constrained the main hydrothermal event in the eastern Río Blanco-Los Bronces-Los Sulfatos block between 8.2 and 4.3 Ma, an interval of about 4 Ma, and associated this mineralization with a 9-km NNW-trending structural corridor where multiple pulses of mineralized porphyritic intrusions and breccias formed the Cu-Mo cluster of Río Blanco-Los Bronces, including Los Sulfatos.

## New geochronological data for the Los Bronces cluster

The new geochronological U-Pb ($n$=6) and $^{40}Ar/^{39}Ar$ ($n$=5) data combined with the first Re-Os ($n$=3) dates obtained from different alteration centers which compose the Los Bronces

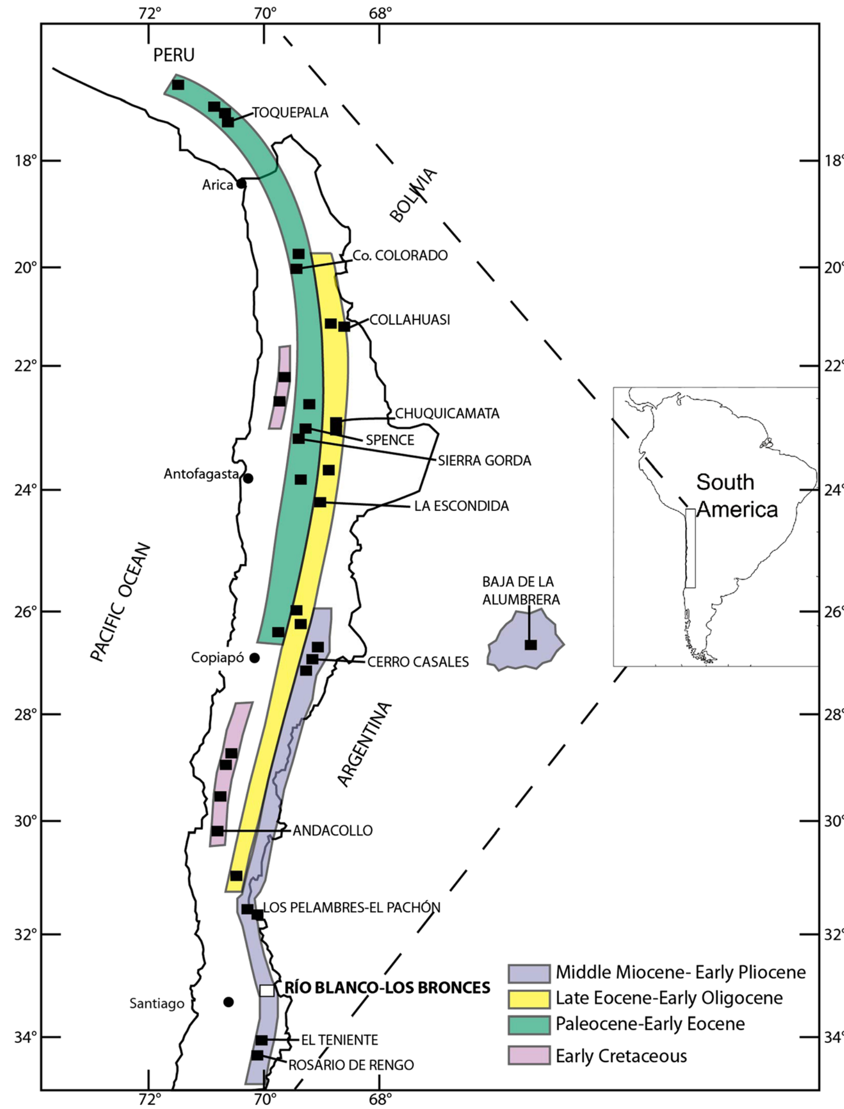


**Fig. 1** Metallogenic belts in central-northern Chile (modified from Sillitoe 1988, 1992)

cluster are presented herein in order of decreasing mineral closure temperature. The alteration centers are from north to south: El Plomo, San Manuel, Los Bonces (LB) open pit, and Los Piches (Figs. 2 and 3). A detailed sample description is given in Table 1; a summary of new ages is given in Table 2. Analytical procedures are summarized in Appendix 1. Complete U-Pb LA-ICPMS, Re-Os, and $^{40}Ar/^{39}Ar$ data are presented in Appendix 2 to 4, respectively.

## U-Pb LA-ICPMS data

El Plomo, at the northern tip of the Los Bronces cluster (Fig. 2), is an isolated alteration area with small outcrops of tourmaline breccias and biotite-altered andesites in the vicinity of multiple quartz-monzonite porphyritic intrusions. Zircons separated from two barren quartz-monzonite rock units (pinkish Plomo-1, greenish Plomo-3) have been dated by the U-Pb LA-ICPMS method. The ages are 10.83±0.11 Ma ($n$=18; MSWD=1.2) and 10.77±0.10 Ma ($n$=19; MSWD=0.73), respectively (Fig. 4a, b). Each age is within the uncertainty of the other.

Two kilometers south of the El Plomo area, a quartz-feldspar porphyry within a sericite-altered zone covering about 6 km$^2$ and associated with a breccia complex, deficient of visible crosscutting relationships, was dated. The zircon sample from the quartz-feldspar porphyry (San Manuel porphyry; SM-2) yields a U-Pb age of 10.19±0.27 Ma (MSWD=1.7; $n$=25) (Fig. 4c). The quartz-feldspatic San Manuel porphyry is similar in texture to the slightly older barren quartz-monzonite porphyries of the northern El Plomo exploration target. This new age range (11–10 Ma) obtained at the northwestern zone of the Los Bronces cluster is characterized by a porphyritic magmatic event that has not been documented from the Río Blanco cluster so far. From the LB open-pit mine, which

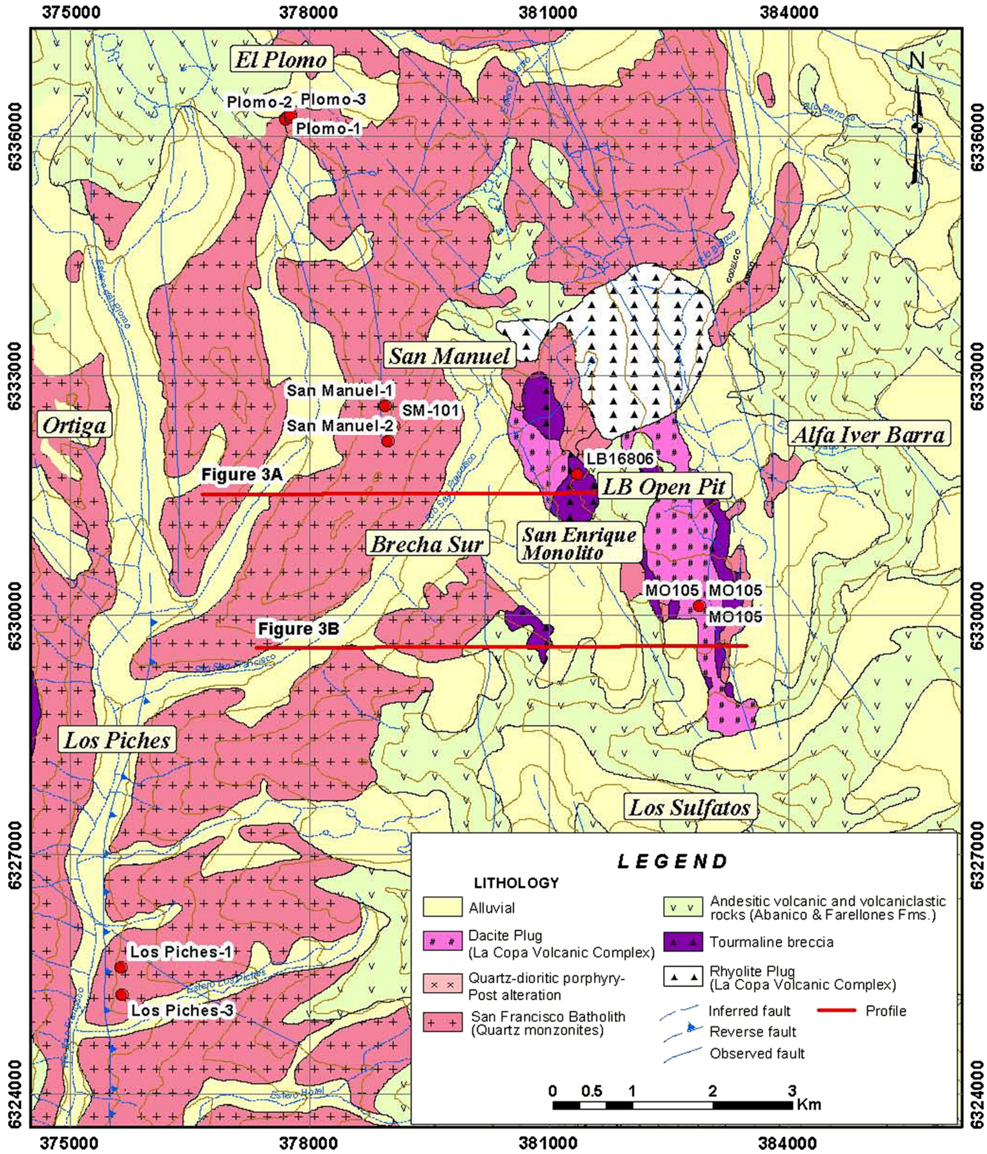


**Fig. 2** Geological map of the Río Blanco-Los Bronces porphyry Cu(-Mo) mega-cluster

includes the mineralized San Enrique Monolito body further southeast (Fig. 2), two drill cores (LB16806 and MO105) were sampled and analyzed by U-Pb LA-ICPMS on zircons (Fig. 4d, e). The biotitized fine-grained equigranular to locally porphyritic quartz monzonite from drill core LB16806 (1,209-1,271 m) yielded a U-Pb zircon crystallization age of 8.49±0.12 Ma (MSWD=1.3; $n$=13; Fig. 4d). This age is equivalent to the petrographically similar Cascada intrusion of the Río Blanco cluster which was dated previously at 8.4±0.23 Ma (U-Pb ID-TIMS; Deckart et al. 2005). Zircons from the MO105 drill core of an intermineral rhyodacitic porphyry (Observatorio Porphyry—3,500 m a.s.l.) with two feldspar types and with disseminated chalcopyrite-pyrite yielded a crystallization age of 6.02±0.13 Ma (MSWD=1.5; $n$=15; Fig. 4e). This age lies within the age range defined by the three mineralized porphyries of the Río Blanco cluster, namely: (1) the quartz-monzonite porphyry (PQM; 7.12 to 6.16 Ma); (2) the feldspar porphyry (PF; 5.84 to 5.17 Ma); and (3) the slightly younger Don Luis porphyry (PDL; 5.23 to 5.08 Ma) (Deckart et al. 2005, 2013).

From the southernmost Los Piches exploration area (Fig. 2), a zircon sample obtained from a small outcrop of white feldspar porphyry with strong phyllic alteration located at the eastern side of the San Francisco river (Fig. 2, Los Piches-3) yielded an age of 13.35±0.10 Ma (MSWD=1.14; $n$=14) (Fig. 4f). This age falls within the age range of 14.7–11.2 Ma given for the San Francisco batholith of the area (Deckart et al. 2005, 2010, 2013; Deckart and Godoy 2006), but represents the oldest porphyry and possibly precursor phase to the economic hydrothermal alteration events recognized so far in the district.

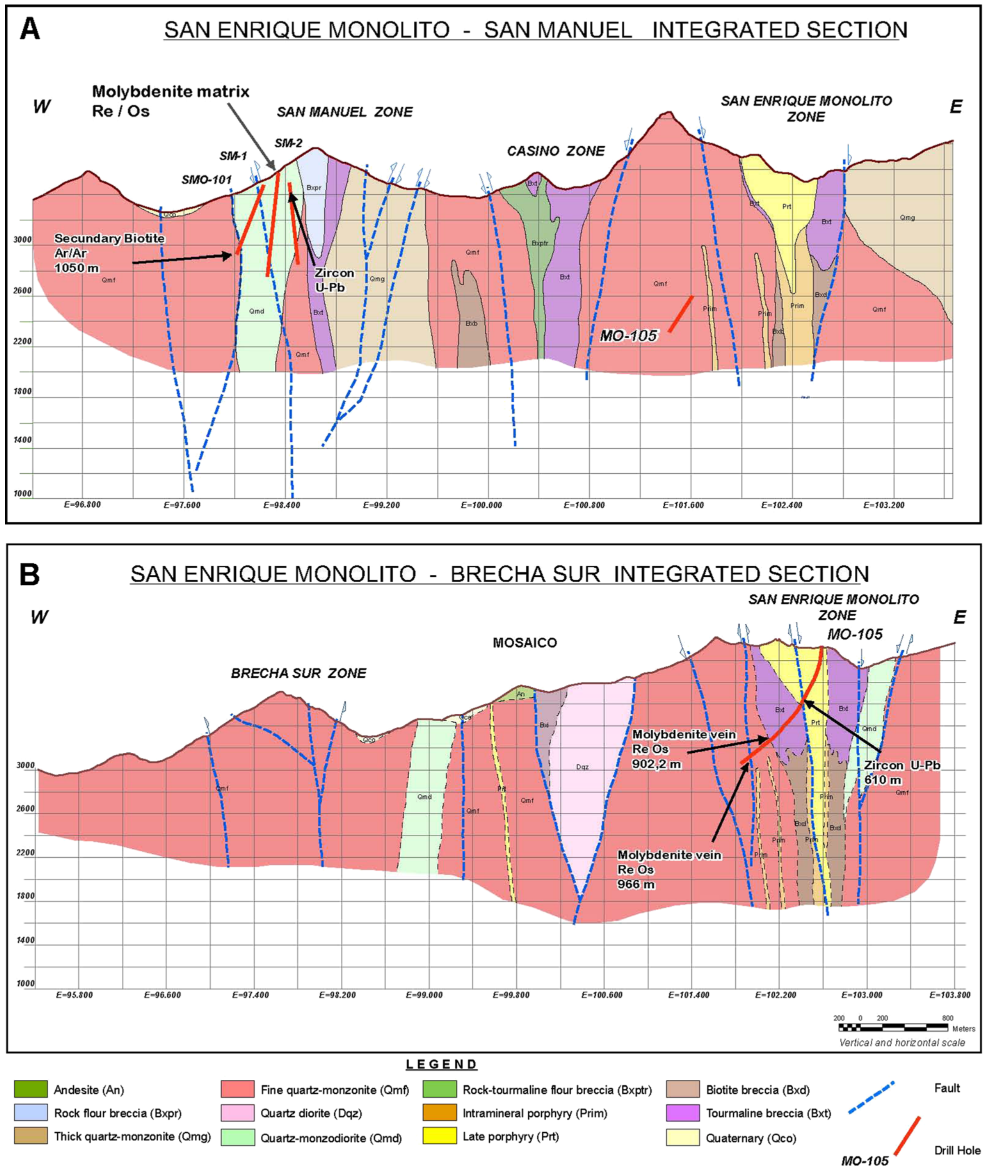


**Fig. 3** Geologic sections through the Los Bronces Mine area. **a** San Enrique Monolito-Brecha Sur integrated section, **b** San Enrique Monolito-San Manuel integrated section

## Re-Os NTIMS data

The breccia complex at the San Manuel target includes at least four varieties: three of them show different types of cement and fragments derived from the San Manuel porphyry and therefore have a maximum age of 10.2 Ma (see above SM-2 U-Pb age, this work). The first is a barren breccia containing potassic feldspar in the groundmass, which is intruded by a mineralized (chalcopyrite-pyrite) tourmaline breccia cemented by secondary chalcocite and by a mineralized quartz-molybdenite-cemented breccia. In map view, all of them are elongated in a NW direction. The fourth type corresponds to a rock-flour matrix breccia with variable quantities of tourmaline clearly post-dating the other minerals, with extensive haloes of sericitic alteration around EW and NE structurally controlled meter-sized bodies. The molybdenite cement of the breccia containing San Manuel porphyry clasts yielded an age of 8.36±0.06 Ma. This age presents an average from a duplicate analysis (8.38±0.04 Ma and 8.34±0.04 Ma) (Appendix 3) and is the oldest so far of the entire Río Blanco-Los Bronces porphyry Cu-Mo cluster, and even older than all molybdenite ages of El Teniente (Maksaev et al. 2004), located 110 km south of Los Bronces within the Mio-Pliocene porphyry Cu (-Mo) belt (Fig. 1). Nevertheless, the late Miocene age of the molybdenite breccia cement conforms to the lithoclasts described in the breccia, and may be coeval with the other two early breccias mentioned above. Furthermore, the breccia formation seems to be constrained to the emplacement of the fine-grained quartz monzonite at depth (8.49±0.12 Ma, LB-16806, this work).

**Table 1** Description of dated samples, Los Bronces cluster

| Rock unit | Sample | Description | Alteration |
|---|---|---|---|
| Plomo-1 | N 6.336.210–E 377.696 3,748 m a.s.l. | Quartz-monzonite porphyry; plagioclase xenocrysts partially to sericite-altered aphanitic groundmass of quartz-K-feldspar; chloritized biotite; scarce opaque and anhydrite | Slight phyllic alteration |
| Plomo-2 | N 6.336.238–E 377.749 3,872 m a.s.l. | Sericite-altered tourmaline breccia; fine-grained quartz-sericite matrix with coarse quartz agglomeration; quartz vein; opaques: limonite, hematite | Strong phyllic alteration |
| Plomo-3 | N 6.336.266–E 377.752 3,864 m a.s.l. | Quartz-feldspar porphyry; feldspar xenocrysts in fine-grained quartz-K-feldspar matrix; epidote partly replacing feldspar; strong chloritization; actinolith; opaques | Phyllic alteration |
| Plomo-4 | N 6.006.470–E 376.697 3,600 m a.s.l. | Biotite-altered andesite; very fine-grained biotite-feldspar matrix; fine biotite veins; invasive secondary biotite; opaques | Strong potassic alteration |
| San Manuel-1 (SM-1) | N 6.332.621–E 378.934 3,765 m a.s.l. | Strong sericitization of the molybdenite-tourmaline breccia; argillites; fine-to-coarse-grained tourmaline; potassic feldspar partly replaced by argillites or sericite; apatite | Sericitization, argillaceous alteration |
| San Manuel-2 (SM-2) | N 6.332.174–E 378.972 3,738 m a.s.l. | Quartz-feldspar porphyry with chloritized biotite, sericitization of plagioclase xenocrysts, biotite with rutile; apatite; calcite; patches of sericite and chlorite | Slight phyllic alteration |
| SM-101 (1,049.5–1,050.2 m) | N 6.332.372–E 379.038 2,613 m a.s.l. | Biotite alteration of fine quartz-monzonite; zones of strong and slight chloritization; biotite with reaction rim; amphibole partially replaced by biotite; calcite; apatite; pyrite-anhydrite veins with sericite halo; disseminated pyrite | Potassic with slight phyllic overprint |
| LB16806 (1,209–1,271 m) | N 6.331.760–E 381.349 2,595 m a.s.l. | Strong biotite alteration in diorite porphyry; slight sericitization of plagioclase xenocryst; some chlorite replacing biotite; anhydrite disseminated pyrite | Potassic alteration with slight phyllic overprint |
| MO105 (608–620 m) | N 6.330.115–E 382.876 3,500 m a.s.l. | Rhyodacitic porphyry with fine-grained quartz-potassic feldspar and chloritized biotite matrix; sericite replacing plagioclase; quartz eyes; fine anhydrite-potassic feldspar-opaques-quartz vein | Slight phyllic alteration |
| MO105 (902.2 m) | N 6.330.115–E 382.876 3,226 m a.s.l. | Fine quartz-monzonite cut by a molybdenite vein with potassic feldspar halo; B-type | – |
| MO105 (965.95–966 m) | N 6.330.115–E 382.876 3,164 m a.s.l. | Fine quartz monzonite with disseminated pyrite cut by a very fine B-type molybdenite vein | – |
| Los Piches-1 | N 6.325.584–E 375.626 2,741 m a.s.l. | Sericite replaced tourmaline breccia; quartz-tourmaline-sericite (-opaques); very fine-grained sericite in agglomeration; no clasts | Strong phyllic alteration |
| Los Piches-2 | N 6.325.242–E 375.639 2,792 m a.s.l. | Sericite replaced tourmaline breccia; sericite-quartz-muscovite-tourmaline(-rutile); scarce actinolith; no clasts | Strong phyllic alteration |
| Los Piches-3 | N 6.325.242–E 375.639 2,792 m a.s.l. | White feldspar porphyry; sericite in quartz-feldspar matrix; plagioclase xenocrystals and matrix strongly seritized; quartz eyes; zones with slight sericitation | Phyllic alteration |

A quartz-molybdenite vein cutting through fine-grained quartz monzonite in the LB open-pit area (MO105, 965.95–966 m; 3,164 m a.s.l.) gave a Re-Os age of 5.35±0.03 Ma. An additional molybdenite sample with less quartz and characterized by a potassium feldspar halo (MO105, 902.2 m; 3,226 m a.s.l.) cuts the same rock unit and yielded an age of 5.65±0.03 Ma. The two B-type vein ages do not overlap within error, but both new ages fall within the molybdenite age ranges indicated for the Río Blanco (5.94–4.89 Ma) and Sur Sur (5.79–5.11 Ma) areas in the Río Blanco cluster (Deckart et al. 2013). The fine-grained quartz monzonite hosting these molybdenite veins has not been dated directly, but it is petrographically similar to the pre-mineral Cascada granodiorite (8.4±0.23 Ma; Deckart et al. 2005) located in the eastern Río Blanco cluster.

## $^{40}Ar/^{39}Ar$ data

$^{40}Ar/^{39}Ar$ analyses have been undertaken on five different samples from the four target zones of the Los Bronces cluster (Fig. 2). Two of these samples are from the northernmost El Plomo exploration area and were taken near the sample sites for the U-Pb analysis (Plomo-1, Plomo-3). The hydrothermal sericite (Plomo-2) of a strongly altered tourmaline breccia yielded a plateau age of 10.58±0.18 Ma (MSWD=0.46; Fig. 5a, b) which constrains the phyllic alteration event of this rock unit. The intensely biotite-altered andesite whole-rock sample (Plomo-4) shows a plateau age of 10.06±0.12 Ma (MSWD=1.4; 100 % of $^{39}Ar$ released; Fig. 5c, d). The plateau represents the age of the potassic alteration event registered in the andesite which is slightly

**Table 2** Geochronology of the dated samples, Los Bronces cluster

| Sample | Sample | Lithology | Dated mineral/ vein | Method | Age±error (Ma) | MSWD | Number of steps/ablations |
|---|---|---|---|---|---|---|---|
| Plomo-1 | N 6.336.210–E 377.696 3,748 m a.s.l. | Quartz-monzonite porphyry | Zircon | U-Pb[a] LA-ICPMS | 10.83±0.11 | 1.2 | 18 |
| Plomo-2 | N 6.336.238–E 377.749 3,872 m a.s.l. | Tourmaline breccia | Sericite | $^{40}Ar/^{39}Ar$[b] | 10.58±0.18 (PA) | 0.64 | 8 |
| Plomo-3 | N 6.336.266–E 377.752 3,864 m a.s.l. | Quartz-feldspar porphyry | Zircon | U-Pb[a] LA-ICPMS | 10.77±0.10 | 0.73 | 19 |
| Plomo-4 | N 6.006.470–E 376.697 3,600 m a.s.l. | Biotite-altered andesite | Whole rock | $^{40}Ar/^{39}Ar$[b] | 10.06±0.12 (PA) | 1.4 | 10 |
| San Manuel-1 (SM-1) | N 6.332.621–E 378.934 3,765 m a.s.l. | Molybdenite-tourmaline breccia | Molybdenite matrix | Re-Os | 8.36±0.06 | – | – |
| San Manuel-2 (SM-2) | N 6.332.174–E 378.972 3,738 m a.s.l. | Quartz-feldspar porphyry | Zircon | U-Pb[a] LA-ICPMS | 10.2±0.3 | 1.7 | 25 |
| SM-101 (1049.5-1050.2 m) | N 6.332.372–E 379.038 2,613 m a.s.l. | Fine quartz monzonite | Secondary biotite | $^{40}Ar/^{39}Ar$[b] | 7.70±0.05 (IIA) | 0.27 | 10 |
| LB16806 (1,209-1,271 m) | N 6.331.760–E 381.349 2,595 m a.s.l. | Diorite porphyry | Zircon | U-Pb[a] LA-ICPMS | 8.49±0.12 | 1.3 | 13 |
| MO105 (608-620 m) | N 6.330.115–E 382.876 3,500 m a.s.l. | Rhyodacitic porphyry | Zircon | U-Pb[a] LA-ICPMS | 6.02±0.13 | 1.5 | 15 |
| MO105 (902.2 m) | N 6.330.115–E 382.876 3,226 m a.s.l. | Fine quartz monzonite | Molybdenite vein | Re-Os | 5.65±0.03 | – | – |
| MO105 (965.95-966 m) | N 6.330.115–E 382.876 3,164 m a.s.l. | Fine quartz monzonite | Molybdenite vein | Re-Os | 5.35±0.03 | – | – |
| Los Piches-1 | N 6.325.584–E 375.626 2,741 m a.s.l. | Tourmaline breccia | Sericite | $^{40}Ar/^{39}Ar$[b] | 12.79±0.31 (IIA) | 0.09 | 5 |
| Los Piches-2 | N 6.325.242–E 375.639 2,792 m a.s.l. | Tourmaline breccia | Sericite | $^{40}Ar/^{39}Ar$[b] | 13.69±0.31 (IIA) | 1.3 | 6 |
| Los Piches-3 | N 6.325.242–E 375.639 2,792 m a.s.l. | White feldspar porphyry | Zircon | U-Pb[a] LA-ICPMS | 13.4±0.1 | 0.32 | 14 |

*PA* plateau age, *IIA* inverse isochron age

[a] U/Pb on zircon single grains

[b] Step heating

younger than the phyllic alteration. This indicates that the potassic alteration of the andesite belongs to a distinctly younger hydrothermal pulse. No direct cross-cutting relationships between the tourmaline breccias, the andesite, and the porphyries were observed. The biotite-altered andesite has been sampled in close distance to the porphyries and the sericite-altered tourmaline breccias.

Additionally, from a long borehole that intercepted the deepest part of San Manuel exploration area, a fine-grained equigranular to locally porphyritic quartz-monzonite unit moderately to intensely altered to secondary biotite-chlorite, with a low content of chalcopyrite-pyrite and bornite intrudes the quartz-feldspar porphyry. The secondary biotite gave a reliable plateau age of 7.73±0.13 Ma (99.4 % of $^{39}Ar$ released; MSWD=0.41) (Fig. 5e, f). The calculated inverse isochron age is 7.70±0.14 Ma (MSWD=0.27; $^{40}Ar/^{36}Ar$ ratio: 299.6±6.7), and both ages are concordant in their two sigma error intervals. Since the age spectrum of the biotite sample shows a slight tendency to older ages in the first steps and the atmospheric ratio is slightly elevated (Fig. 5e, f), the inverse isochron age is the recommended age of the secondary biotite alteration event at San Manuel. The potassic alteration at both El Plomo and San Manuel is suggested to be locally restricted and not affected by the later fluid flow and thermal disturbance.

Looking to the southern exploration area of Los Piches (Fig. 2), two sericite samples were analyzed to obtain information on the phyllic alteration event in that part of the cluster. A few tens of meters above the 13.4 Ma porphyritic white feldspar porphyry (see above), a strongly sericite-altered tourmaline breccia with obliterated clasts was sampled, and a sericite $^{40}Ar/^{39}Ar$ plateau age (Los Piches-1) of 12.88±0.08 Ma (MSWD=0.12; 58.2 % $^{39}Ar$ released) was obtained. The inverse isochron age calculated on the same plateau steps is 12.79±0.31 Ma (MSWD=0.09) and indicates a slightly elevated $^{40}Ar/^{36}Ar$ ratio of 310±55 compared to the atmospheric value (Fig. 5g, h). The recommended phyllic alteration age is therefore the inverse isochron age.

On the western side of the San Francisco river (Fig. 2), sericite from the second tourmaline breccia (Los Piches-2)

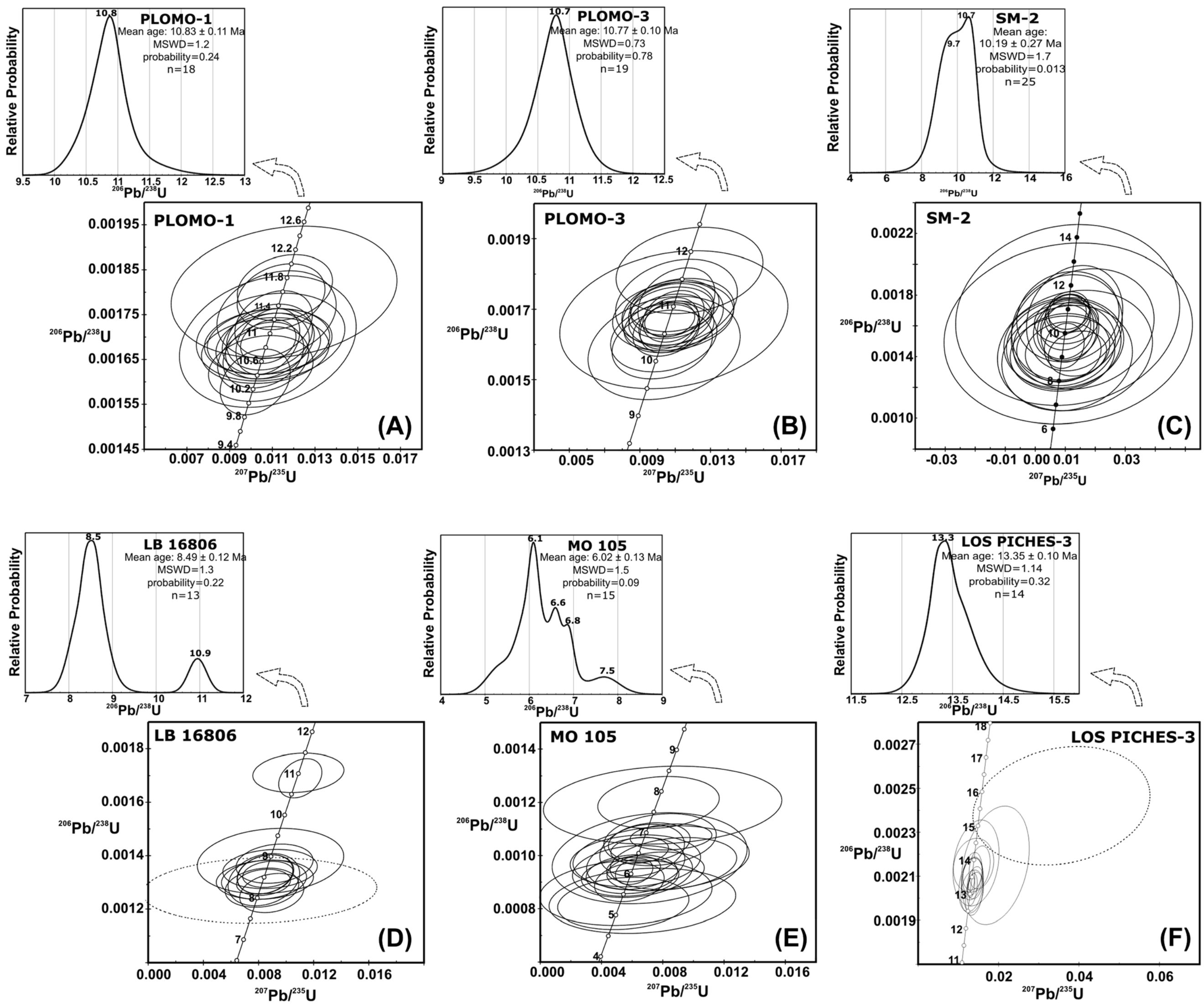

**Fig. 4** Terra Wasserburg, mean $^{206}Pb/^{238}U$ ages, and relative age probability diagrams. (**a**)–(**b**) El Plomo area, (**c**) San Manuel area, (**d**)–(**e**) LB open pit, and (**f**) Los Piches area

with clasts of an unidentified quartz monzonite has a plateau age of 13.89±0.22 Ma (MSWD=1.7; 98.8 % $^{39}Ar$ released). The calculated inverse isochron age is 13.69±0.31 Ma (MSWD=1.3; $^{40}Ar/^{36}Ar$ ratio 309±15) (Fig. 5i, j). The inverse isochron and plateau ages of this sample are concordant. Nevertheless, the inverse isochron age is preferred since the atmospheric value is slightly increased which might indicate that the plateau overestimates the age of the event. However, both sericite ages (Los Piches-1 and Los Piches-2) on distinct tourmaline breccias of the same area gave clearly distinct ages that do not overlap within analytical uncertainty. Nevertheless, each analysis indicates a slight excess $^{40}Ar$ component in the spectra, suggesting that the ages are maximum ages for the phyllic alteration. The older sericite of the tourmaline breccia (Los Piches-2) was taken at a distance of a few meters from the white feldspar porphyry (Los Piches-3), while the younger sericite sample (Los Piches-1) was taken from a tourmaline breccia within a vertical distance of 50 m and a horizontal N-S distance of about 240 m from Los Piches-2 and Los Piches-3. These sericite ages are slightly older than the $^{40}Ar/^{39}Ar$ age of 12.3±0.1 Ma obtained on a lithocap with hypogene alunite located 3 km NW in the Ortiga Valley (Eggers 2009; Fig. 2). Since the new sericite ages are affected by excess $^{40}Ar$, they may be coeval with the alunite in the lithocap or somewhat older. Irrespective of that, the ages on phyllic alteration registered at the Río Blanco-Los Bronces porphyry Cu(-Mo) mega-cluster indicate that at least two hydrothermal events have affected the area. The first, apparently nonmineralizing event, at around 13–12 Ma, and second, economic event around 8.5–4.5 Ma.

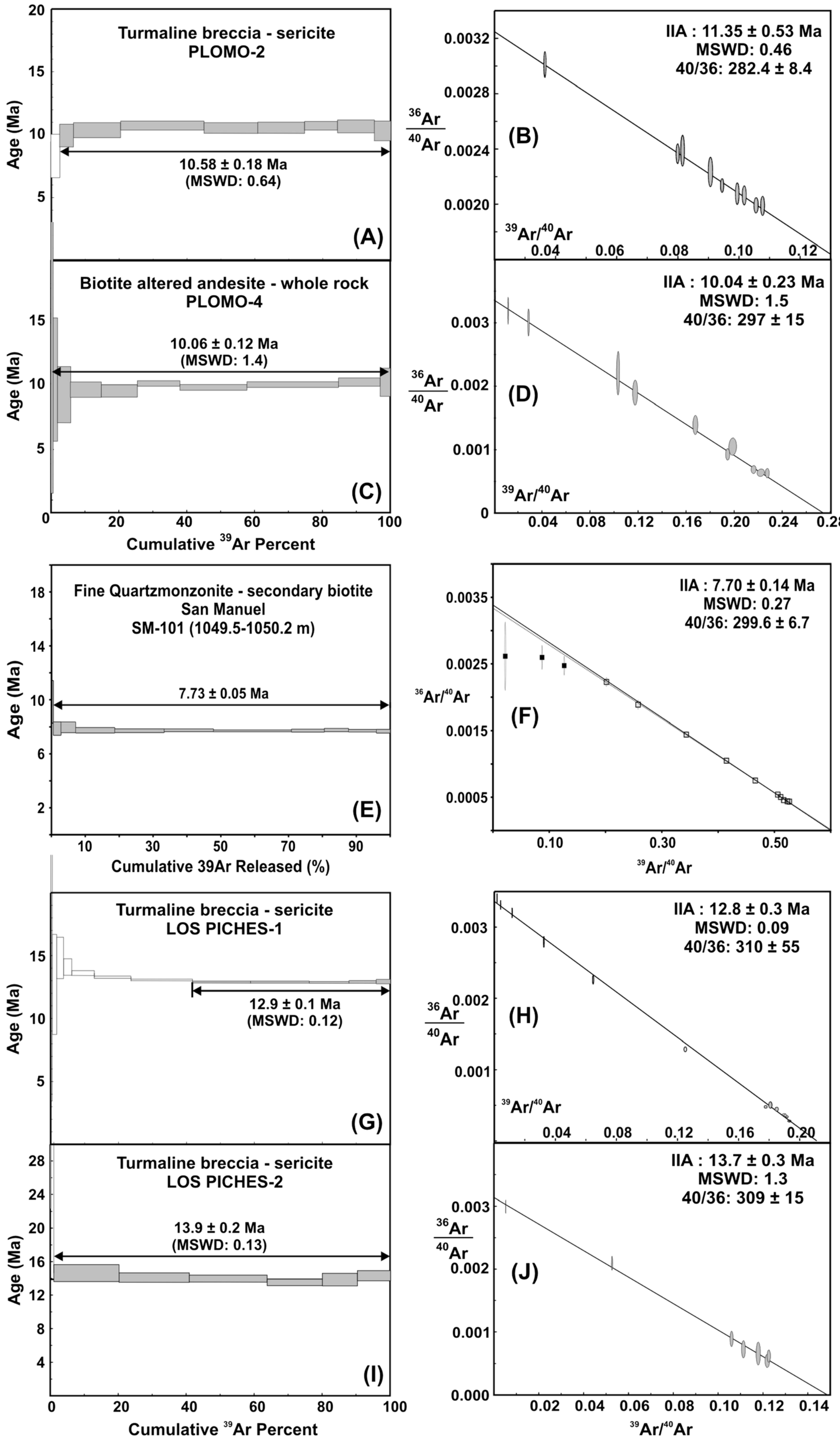


**Fig. 5** $^{40}Ar/^{39}Ar$ age spectra and inverse isochron diagrams with corresponding ages on hydrothermal biotite and sericite. Obtained results on (**a**)–(**d**) El Plomo, (**e**) and (**f**) San Manuel, and (**g**)–(**j**) Los Piches exploration areas

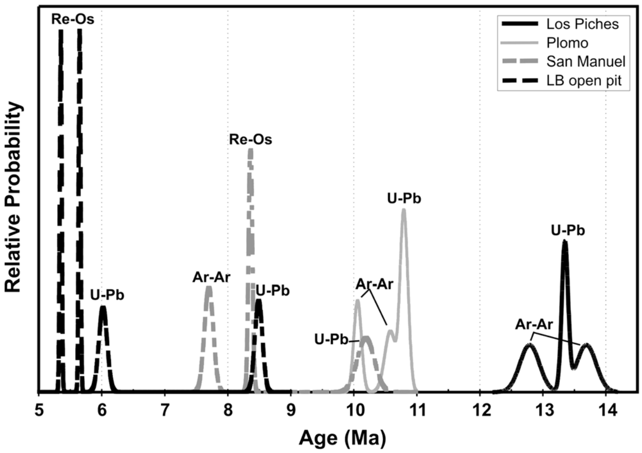


**Fig. 6** Relative age probability diagram representing the entire set of obtained U-Pb, Re-Os, and Ar-Ar age data including their analytical uncertainties

## Implications of the new geochronologic data

The new geochronologic data, their time, and spatial distribution at Los Bronces (Fig. 6) show a major difference compared to the Río Blanco counterpart and El Teniente porphyry Cu-Mo deposits: First, the porphyritic intrusion in the Los Piches exploration area of 13.4± 0.1 Ma (Los Piches-3) and its associated sericite alteration represent the oldest evidence for hydrothermal activity in the entire Río Blanco-Los Bronces district, albeit devoid of economic Cu, Mo, or Au mineralization. Second, the oldest mineralization age, represented by molybdenite in breccia cement from the San Manuel exploration area 1.5 km NW of the limit of the LB open pit, is 8.36 Ma. Moreover, a general Ar/Ar age resetting event, as documented in the Río Blanco cluster, could not be recognized at Los Bronces. Here, $^{40}Ar/^{39}Ar$ ages usually reflect hydrothermal mineral formation related to their corresponding local porphyry intrusive event.

### Regional and local considerations

The Río Blanco-Los Bronces cluster is located in the middle between the Los Pelambres-El Pachón (about 31°42’ S) and the El Teniente porphyry copper districts located about 110 km to the north and south, respectively (Fig. 1). Re-Os molybdenite dates from Los Pelambres-El Pachón show, for the northwestern portion at Los Pelambres, an age range of 11.7 to 11.0 Ma (Bertens et al. 2006) and, for the southeastern portion at El Pachón, slightly younger ages of 9.16 Ma and 8.43 Ma (Bertens et al. 2006). Thus, the Los Pelambres-El Pachón district shows a similar age distribution as the one recognized at Río Blanco-Los Bronces, namely, older alteration events located in a NNW-trending corridor further to the west with a tendency to younger ages up to the main mineralization-alteration events at around 6–5 Ma in the central-eastern part of the mega-cluster. This age distribution pattern has not been observed at El Teniente further to the south in the Mio-Pliocene metallogenic belt (Fig. 1).

Between the Los Pelambres-El Pachón and Río Blanco-Los Bronces districts, poorly age-constrained fine-grained quartz-monzonite and diorite intrusive centers of ca. 8–8.5 Ma age have been recongized (Toro et al. 2006). In contrast, south of Río Blanco-Los Bronces, no Re-Os molybdenite ages in the 8–9 Ma range have been published. South of the El Teniente district, at the Rosario de Rengo porphyry Cu(-Mo) prospect, two U-Pb ages have been obtained on mineralized porphyries yielding 8.43± 0.15 and 8.02±0.09 Ma (Muñoz 2008). However, no Re-Os or other geochronological data have been published from this area, and further work is necessary to unequivocally constrain the mineralization age range for the southernmost extension of this metallogenic belt.

$^{40}Ar/^{39}Ar$ secondary biotite and sericite ages of the different areas of the Los Bronces cluster seem to not have been affected by subsequent hydrothermal fluid circulation as postulated to be responsible for the restricted $^{40}Ar/^{39}Ar$ ages on hydrothermal K-silicates (5.31–4.24 Ma) for the Río Blanco cluster (Deckart et al. 2013). Consequently, hydrothermal fluid flow was probably restricted to separate blocks belonging to a NW-oriented structural corridor since large-scale thermal disturbance and fluid flow would have uniformly reset the Ar/Ar ages. As suggested by Carrizo et al. (2012), the hydrothermal activity that formed this giant district occurred along NW-oriented faults which are the result of differential regional N-S shortening. It is proposed that this preferential NW-NNW direction gave rise to a structural corridor which hosts the different hydrothermal pulses and breccias and produced dislocation of distinct areas in the entire cluster. It is worth noting that San Manuel is situated on an uplifted structural block compared to the rest. In this context, this area was probably not affected by the general resetting between 5.3 and 4.2 Ma which affected the Río Blanco portion of the mega-cluster (Deckart et al. 2005, 2013), perhaps because it was already at higher levels and out of the reach of fluids hot enough (280±20 °C) to reset the Ar systematics in biotite and the 7.7 Ma age (this work), or lateral fluid flow of distinct hydrothermal pulses was locally restricted.

The 8.36 Ma molybdenite age for Los Bronces likely represents a hydrothermal event apparently restricted to Los Bronces or not yet recognized in the Río Blanco part of the porphyry cluster nor in the El Teniente porphyry Cu(-Mo) deposit where molybdenite ages range from 6.30–4.42 Ma (Maksaev et al. 2004; Deckart et al. 2013; Mathur et al. 2001).

U-Pb zircon ages are increasingly older with distance from the productive nucleus of the Los Bronces and Río Blanco cluster. In contrast, $^{40}Ar/^{39}Ar$ alteration ages are at least in part diachronic within different lithologies at the Río Blanco cluster, whereas distinct Re-Os ages are attributed to specific localized mineralization centers.

The new ages for the porphyry intrusions at San Manuel, El Plomo, and Los Piches of the Los Bronces cluster are coeval with the entire magmatic pulses affecting the central Andean Cordillera. U-Pb emplacement ages between 15–10 Ma have been documented, e.g., in Los Pelambres (Bertens et al. 2003, 2006), the San Francisco batholith (Deckart et al. 2005, 2013), Portillo and the Juncal river intrusions (Montecinos et al. 2008), La Gloria stock, and Cerro Mesón Alto massif (Deckart et al. 2010).

## Conclusions

The new geochronological data set using U-Pb LA-ICPMS, Re-Os, and $^{40}Ar/^{39}Ar$ techniques on four hydrothermally altered areas at the Los Bronces cluster confirms what was already suggested for the Río Blanco counterpart, i.e., that alteration and mineralization are diachronous across the district. This observation is most probably due to the presence of a long-lived batholithic magma chamber beneath the Río Blanco-Los Bronces district which episodically became rejuvenated and giving rise to visibly distinct barren and fertile pulses of porphyry intrusions. On a regional scale, these late Miocene to early Pliocene magmatic pulses are also recognized in the entire central Andean zone between 31–34° S.

The new U-Pb and Re-Os ages on zircon and molybdenite, respectively, from the Los Bronces mining area (open pit, nucleus of the mine) are overall concordant with U-Pb and Re-Os ages obtained at the Río Blanco cluster. Intrusions at Los Piches, located at the southern limit of the Los Bronces district, are the oldest of all four areas studied and were emplaced in two episodes, at 14.7 and 11.3 Ma. The younger of these two magmatic pulses is slightly older than the 10.8 Ma porphyry intrusion at El Plomo, located at the northernmost tip of the district and the 10.2 Ma San Manuel porphyry in the center-west of the district. The latter, San Manuel, is contemporaneous with phyllic and potassic alteration events recognized in the El Plomo sector. Phyllic alteration occurred in at least two separate hydrothermal events, namely: the first and barren one at 13–12 Ma and the second and mineralized one at 8.4–4.5 Ma.

The oldest Re-Os age of 8.36±0.06 Ma from molybdenite cement of a molybdenite-quartz breccia in the San Manuel area of the Los Bronces district is 2.2 Ma older than the oldest Re-Os age for Río Blanco and expands the range of mineralization ages to 8.4 Ma in the district but coincides with the oldest biotite age related to mineralization. Early molybdenite mineralization at Los Bronces predated hydrothermal activity in the Río Blanco part of the cluster, but was coeval with the barren Cascada granodiorite and Diorite at Río Blanco. This new molybdenite breccia cement age is 2.1 Ma older than molybdenite ages for the El Teniente porphyry Cu (-Mo) deposit which, so far, has generally been considered coeval with the Río Blanco-Los Bronces cluster.

The general space-time evolution of intrusive and hydrothermal activity from older in the west to younger towards the east in the Río Blanco-Los Bronces district is similar to the overall pattern documented for the Los Pelambres-El Pachón porphyry Cu-Mo (-Au) district.

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