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LETTER

Late Carboniferous porphyry copper mineralization at La Voluntad, Neuquén, Argentina: Constraints from Re–Os molybdenite dating

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Abstract The La Voluntad porphyry Cu–Mo deposit in Neuquén, Argentina, is one of several poorly known porphyry-type deposits of Paleozoic to Early Jurassic age in the central and southern Andes. Mineralization at La Voluntad is related to a tonalite porphyry from the Chachil Plutonic Complex that intruded metasedimentary units of the Piedra Santa Complex. Five new Re–Os molybdenite ages from four samples representing three different vein types (i.e., quartz–molybdenite, quartz–sericite–molybdenite and quartz–sericite–molybdenite ± chalcopyrite–pyrite) are identical within error and were formed between ~312 to ~316 Ma. Rhenium and Os concentrations range between 34 to 183 ppm and 112 to 599 ppb, respectively. The new Re–Os ages indicate that the main mineralization event at La Voluntad, associated to sericitic alteration, was emplaced during a time span of 1.7±3.2 Ma and that the deposit is Carboniferous in age, not Permian as previously thought. La Voluntad is the oldest porphyry copper deposit so far recognized in the Andes and indicates the presence of an active magmatic arc, with associated porphyry style mineralization, at the proto-Pacific margin of Gondwana during the Early Pennsylvanian.

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Introduction

The Andean Cordillera is probably the most important copper province in the world with several world-class porphyry copper, IOCG, and manto-type deposits (e.g., Camus 2003; Sillitoe and Perelló 2005). The La Voluntad deposit is one of 13 porphyry Cu–Mo systems of Paleozoic to Early Jurassic age (Fig. 1) recognized so far in the central and southern Andes (Camus 2003). The deposit is located 74 km SW of Zapala and is part of the Sierra de Chachil, Neuquén, Argentina. The deposit was discovered ca. 1974 by the Dirección Nacional de Fabricaciones Militares, Argentina, as part of an exploration program that included geochemical and geophysical exploration, as well as three diamond-core drill sites (Sabalúa 1975). The results of this exploration program identified a small low-grade (0.1–0.2% Cu) porphyry Cu deposit of possible Late Cretaceous age. Sillitoe (1977) reported a Permian age (K–Ar of 281±4 Ma) on biotite from the tonalite porphyry, whereas Ugalde and Vivallo (1996) reported a sericite K–Ar age of 295±7 Ma.

Because of its high rhenium and osmium content, molybdenite has proven to be an accurate and precise geochronometer (e.g., McCandless and Ruiz 1993; Barra et al. 2003, 2005; Valencia et al. 2006). In this contribution, we have used the Re–Os isotopic system on several molybdenite samples from different vein types to resolve the age of molybdenite deposition and, by inference, the age of formation of this deposit, and to estimate the duration of the hydrothermal mineralization system. The

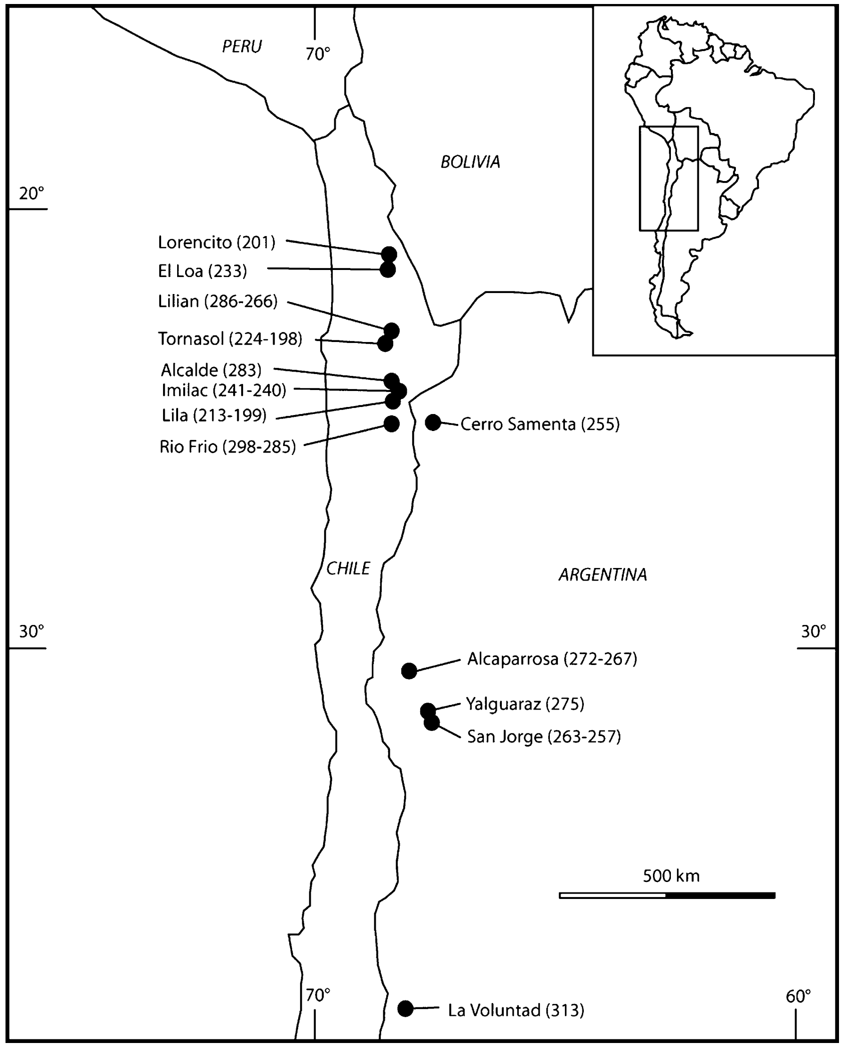

Fig. 1 Location of Late Paleozoic to Early Jurassic porphyry copper deposits of the Andes of Chile and Argentina. *Numbers in parenthesis* after deposit names are K–Ar ages taken from Sillitoe (1977), Camus (2003), and Sillitoe and Perelló (2005). Age for La Voluntad is Re–Os molybdenite age from this study

results presented here also provide insights on the tectonic evolution of the Gondwana margin during the Paleozoic.

Geologic setting

The basement in the area is composed of polydeformed metamorphic rocks (schists, minor gneisses, and migmatites) of the Paleozoic Piedra Santa Complex (Digregorio and Uliana 1980; Franzese 1995). The Piedra Santa Complex is intruded by the Chachil Plutonic Complex, which comprises a series of calc–alkaline stocks ranging from gabbro to granite (Garrido and Domínguez 1997; Franzese et al. 2006). These metamorphic and igneous units represent the Paleozoic magmatic arc on the proto-Pacific margin of Gondwana. Continental extension events during the Late Triassic to Early Jurassic resulted in the development of the Neuquén back-arc basin. Syn-rift accumulations are represented by volcanic and sedimentary units of the Lapa Formation (Franzese et al. 2006). The Lapa Formation is overlain by siliciclastic and carbonate deposits of the Chachil and Sierra Chacaico Formations, both representing shallow marine depositional conditions. These formations grade upward to a thick sequence of black shales and turbidites of Los Molles Formation (Fig. 2), which reflect deep marine sub-oxic conditions and further marine flooding during the Early Jurassic (Burgess et al. 2000; Franzese et al. 2006). The Cretaceous is represented in the area by the sedimentary La Amarga and Bajada Colorada Formations, and is covered by several Tertiary volcanic units (Fig. 2).

Local geology

The geology of the La Voluntad area has been described by Garrido and Domínguez (1997). The area is characterized by granodiorite that is intruded by a tonalite porphyry stock and a series of dikes of different composition (Fig. 3). The granodiorite is composed of quartz, feldspar, biotite, and

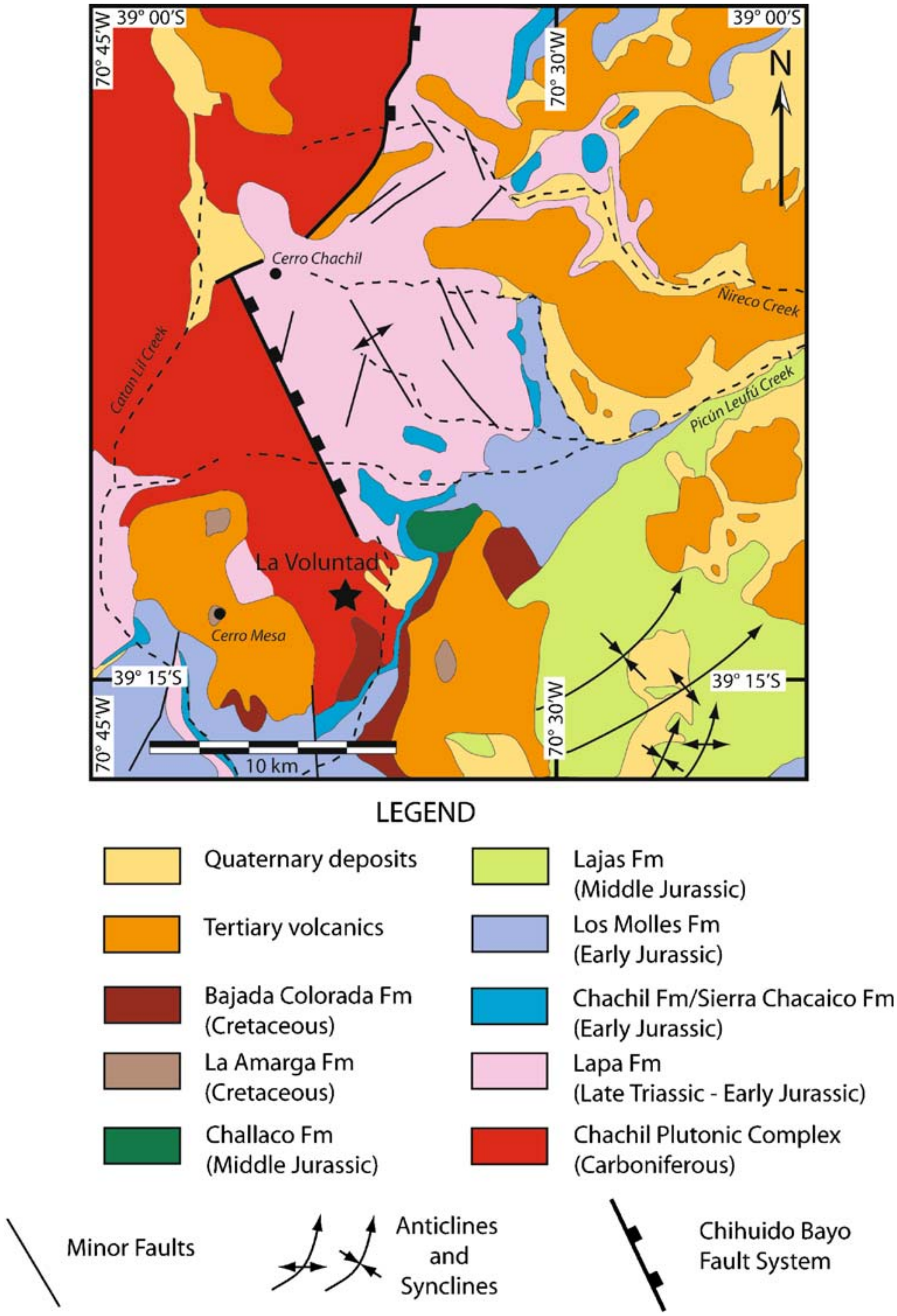

Fig. 2 Geologic map of the La Voluntad area. Adapted from Garrido and Domínguez (1997) and Franzese et al. (2006)

amphibole, and shows textural variations from porphyritic to equigranular and minor hydrothermal alteration. The contact between the granodiorite and the tonalite porphyry is gradational. The tonalite has a porphyritic texture and is composed of quartz, plagioclase, and biotite. This tonalite porphyry stock is possibly genetically related to the intermediate or late stage of the Chachil Plutonic Complex. Late diabase and aplitic dikes intrude both the granodiorite and the tonalite porphyry units.

Mineralization and alteration are centered on the tonalite porphyry. All three major alteration styles (i.e., potassic, sericitic, and propylitic alteration) are recognized at La Voluntad. Potassic alteration is best developed at the central area of the tonalite porphyry. It is represented mainly by patches of secondary biotite with subordinate K-feldspar, quartz, minor sericite, and disseminated pyrite, chalcopyrite, and traces of molybdenite. Potassic alteration is also present at the periphery of the tonalite porphyry as sparse irregular and discontinuous

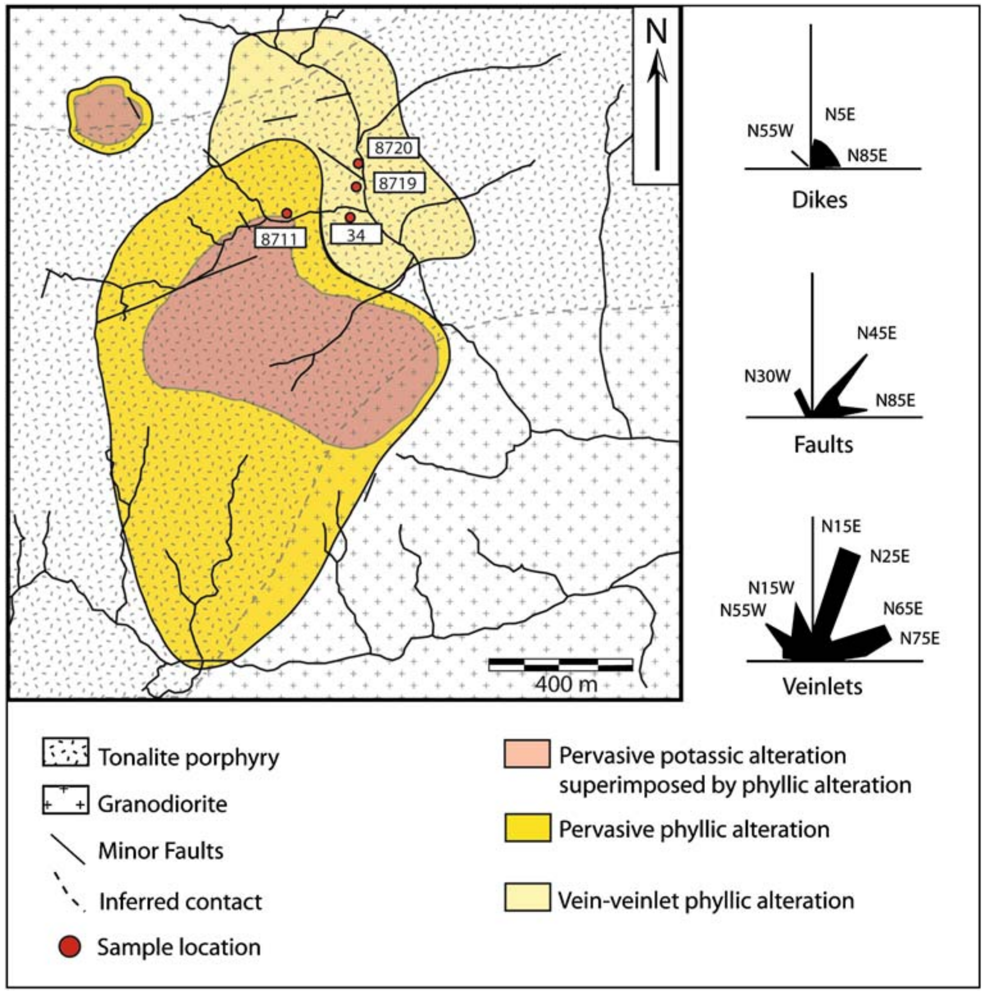

Fig. 3 Simplified geologic map of the La Voluntad porphyry Cu–Mo system, showing the location of dated samples. Modified after Garrido and Domínguez (1997)

veinlets of several mineral assemblages such as biotite, biotite–quartz, K-feldspar–quartz, biotite–K-feldspar–quartz, biotite–quartz–molybdenite, and biotite–quartz–sericite–molybdenite (Garrido and Domínguez 1997). The potassic alteration is overprinted by later superimposed sericitic alteration (Fig. 3). The sericitic alteration is the most extensive, and several vein alteration assemblages have been identified (e.g., quartz, quartz–sericite, quartz–pyrite, quartz–molybdenite, quartz–sericite–molybdenite, and quartz–sericite–sulfides). Prophylitic alteration (chlorite, calcite, epidote, and zeolites) is less developed and mostly represented by alteration of mafic minerals (biotite and amphibole) by chlorite and minor epidote (Garrido and Domínguez 1997). Sulfide mineralization is mostly associated to the sericitic alteration, and it is represented by pyrite, chalcopyrite with minor molybdenite, arsenopyrite, sphalerite, wolframite, and traces of bornite. Supergene mineralization is scarce and present as oxides (Cu oxides and limonites) and minor secondary copper sulfides (chalcocite and covellite).

Fluid inclusion studies performed on quartz from veins associated to the potassic and sericitic alteration zones showed homogenization temperatures in the range of 240–420°C and low salinities (<12 wt% equivalent of NaCl; Ugalde and Vivallo 1996; Garrido and Domínguez 1997).

Geochronological information on La Voluntad deposit is limited with only two reports published. Sillitoe (1977) dated a biotite sample from the tonalite porphyry using the K–Ar method (281±4 Ma), and Ugalde and Vivallo (1996) reported a K–Ar age of 295±7 Ma for sericite associated to the phyllic alteration.

Sampling and analytical techniques

Although molybdenite is present in both potassic and sericitic vein assemblages in the potassic zone, it is usually scarce. Four molybdenite samples representing three different vein types from the sericitic alteration zone (i.e., quartz–molybdenite, quartz–sericite–molybdenite, and quartz–sericite–molybdenite ± chalcopyrite–pyrite) were selected for Re–Os dating. Sample locations, vein type, and associated alteration of samples analyzed are given in Table 1.

The Re–Os analytical procedure used in this study is described in Barra et al. (2003). About 20 to 40 mg of fine-

Table 1 Description of molybdenite samples from La Voluntad

Sample	Location (UTM coordinates)	Description
34	5659631 N–361043° E	Sericitic alteration, quartz-molybdenite vein in tonalite porphyry
8711	5659649 N–360820° E	Sericitic alteration, quartz-sericite-molybdenite ± chalcopyrite-pyrite vein in tonalite porphyry
8719	5659688 N–361103° E	Sericitic alteration, quartz-sericite-molybdenite vein in tonalite porphyry
8720	5659773 N–361115° E	Sericitic alteration, quartz-molybdenite ± sericite vein in tonalite porphyry

All coordinates are UTM zone 19.

grained molybdenite were dissolved and equilibrated with ^{190}Os and ^{185}Re spikes in a Carius tube with 8 ml of a 3:1 mixture of HNO_3 and HCl (Shirey and Walker 1995). About 2 ml of hydrogen peroxide was added to ensure complete oxidation and equilibration. The tube was heated to 220°C for 24 h. Os was extracted using the procedure described by Nägler and Frei (1997) and purified by microdistillation, and Re by a two-stage column using AG1-X8 resin. Total procedure blanks are 4±2 and 20±15 pg for Os and Re, respectively.

Samples were analyzed by negative thermal ionization mass spectrometry (Creaser et al. 1991; Völkening et al 1991) on a VG Sector 54 mass spectrometer with Faraday cups in static mode. Ages are reported with a 0.5% error, which is a conservative estimate and includes all sources of error (i.e., uncertainty in the Re decay constant, weighing, Re and Os spike calibrations, and analytical errors) and considered equivalent to a 2σ.

Results

Five analyses of four molybdenite samples are reported in Table 2. Total rhenium and ^{187}Os concentrations vary in the range 34–183 ppm and 112–599 ppb, respectively. A replicate analysis was performed on sample 34, and the ages obtained were identical within error (Fig. 4). These five Re–Os molybdenite ages range between ~312 to 316 Ma and are older than two previous K–Ar ages that range between 277 and 302 Ma (Sillitoe 1977; Ugalde and Vivallo 1996).

Discussion

Compared to the Cenozoic porphyry Cu–Mo deposits of the central Andes, the porphyry deposits of Late Paleozoic to early Mesozoic are poorly studied. The relative low ore grades (<0.2% Cu) and the lack of significant secondary enrichment, possibly due to environmental conditions and/or erosion, bestow upon these uneconomic deposits only a scientific interest. Understanding these Paleozoic porphyry deposits can help to understand the tectonic evolution of the proto-Pacific margin of Gondwana during the Paleozoic. All of the 13 known porphyry type deposits of the Late Paleozoic to early Mesozoic belt (i.e., Lorencito, 201 Ma; El Loa, 233 Ma; Lilian, 286–266 Ma; Tornasol, 224–198 Ma; Lila, 195–213 Ma; Alcalde, 283 Ma; Imilac, 241 Ma; Rio Frio, 298–285 Ma; Cerro Samenta, 255 Ma; Alcaparrosa, 267–272 Ma; Yalguaraz, 275 Ma; San Jorge, 270–257 Ma; La Voluntad, 281–295 Ma) have been dated mostly using only the K–Ar method (Camus 2003; Sillitoe and Perelló 2005). K–Ar data usually have an associated error in the range of 1–3% of the age determination, and the isotopic system can be subject to resetting or Ar loss. The large range of ages reported for some deposits (e.g., Tornasol, ~20 Ma) suggests that the system was disturbed because most porphyry systems are formed during a period that ranges between <1 to 8 m.y. (i.e., Barra et al. 2005). In comparison, the Re–Os system applied to molybdenite yields results with an associated error between 0.33% to ~1% of the age determination. The Re–Os system, like all isotopic systems, can be disturbed under different conditions (see Barra et al. 2003 and 2005, for discussion). The consistency of the determined ages of different samples and the replicate of sample 34 indicates that the Re–Os system was not disturbed in the samples analyzed in this study.

The new Re–Os ages for molybdenite from different vein types of the sericitic alteration zone show that the main

Table 2 Re–Os data for molybdenite from the La Voluntad porphyry Cu–Mo deposit

Sample	Weight (g)	Total Re (ppm)	^{187}Re (ppm)	^{187}Os (ppb)	Age (Ma)
34–1	0.034	135.3	84.7	443.3	313.4±1.6
34–2	0.039	142.0	88.9	467.2	314.6±1.6
8711	0.040	71.7	44.9	235.0	313.3±1.6
8719	0.021	34.0	21.3	111.7	313.9±1.6
8720	0.037	183.1	114.6	599.3	312.9±1.6

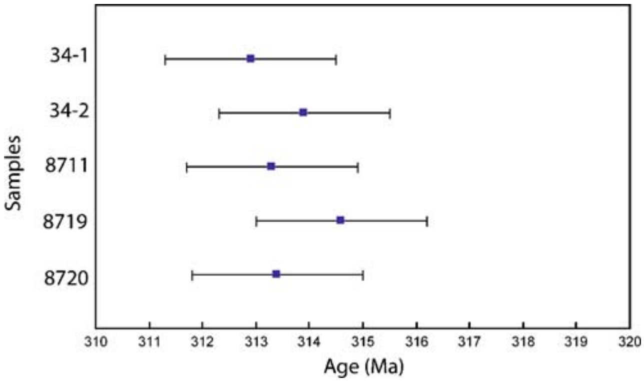

Fig. 4 Summary of Re–Os molybdenite ages. Error bars are 0.5% of the age determination and are equivalent to a 2-sigma level

pulse of mineralization occurred at a restricted period of time. Unfortunately, molybdenite from the potassic alteration could not be dated, and hence, the overall longevity of the porphyry system remains unknown, but it is unlikely that the porphyry system at La Voluntad remained active for more than a few million years.

The new Carboniferous age of La Voluntad is significantly older than previous K–Ar ages that indicated a Permian age. Regardless, La Voluntad still remains the oldest porphyry system described so far in the South American porphyry province. This new age provides some constraints on the tectonic setting of the Pacific margin of Gondwana during the Early Pennsylvanian and indicates the presence of a magmatic arc, with associated porphyry style mineralization, at the proto-Pacific margin of Gondwana during the Early Pennsylvanian. This magmatic arc was emplaced over thin continental crust (<40 km) and extended from southern Argentina to northern Chile (Fig. 5; Mpodozis and Kay 1992). Paleogeographic reconstructions show that the La Voluntad porphyry was emplaced at a high latitude (~52° S) and was most probably, at that time, partially or completely covered by polar ice.

Conclusions

Four molybdenite samples associated to the sericitic alteration zone yielded identical Re–Os ages within error and where emplaced during a time span of 1.7±3.2 m.y. These new Early Pennsylvanian ages of La Voluntad are significantly older than previous K–Ar ages that indicated a Permian age. The new data is consistent with the presence

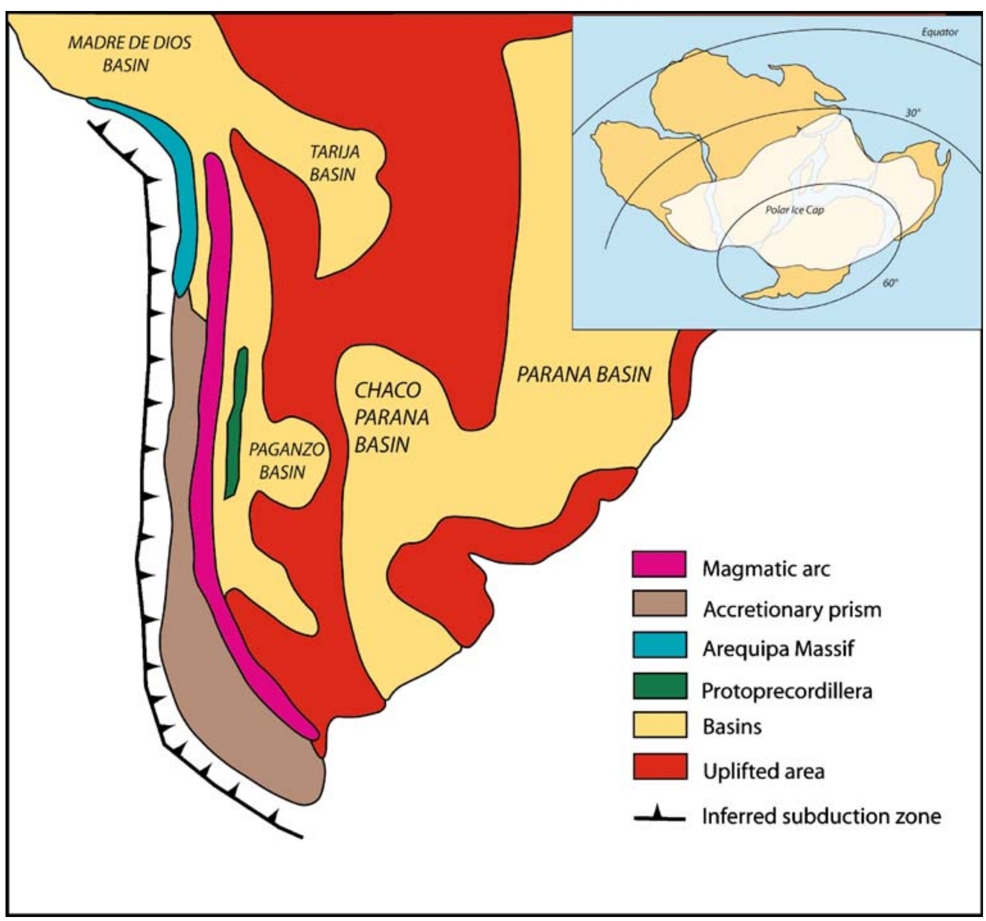

Fig. 5 Paleotectonic reconstruction of southern South America in the Carboniferous–Permian (modified from Mpodozis and Ramos 1989; Limarino and Spalletti 2006). *Inset* shows the location of Gondwana and estimated extension of polar ice during the Carboniferous

of a magmatic arc, with associated porphyry style mineralization, that extended from southern Argentina to northern Chile at the proto-Pacific margin of Gondwana during the Late Carboniferous.

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