Re-Os ages of molybdenites associated with granites of the North Patagonian Batholith, Chilean Andes

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INTRODUCTION

The Northern Patagonian Andes is a distinctive segment of the South American continental margin. Its geological evolution is different to the evolution of other segments to the north and its metallogenic evolution is poorly studied. Geodynamic processes involved in the evolution of the Northern Patagonian Andes are not well constrained, but they certainly played a relevant role during its metallogenetic evolution.

Mineral occurrences and mineral deposits of medium to small size have been reported in the Patagonian Andes. They are not as abundant as in the Central Chilean Andes, although the favorable tectonic setting (subduction plate margin) for ore deposit genesis, which is common in all Chilean Andes at least since Jurassic times, is also present in the area.

The area of study is located in the Chilean Andes between 41-44° S (Figure 1). Based on the ore deposit types and spatial and temporal distribution of the mineralization, two metallogenic belts, separated by the Liquiñe-Ofqui fault zone, are recognized in this segment (Duhart *et al.*, 2000): a Lower Cretaceous Polymetallic Belt and a Miocene Gold Belt (Figures 1 and 2). In both belts, molybdenite occurrences have been reported in association with monzogranitic and tonalitic stocks, respectively (Figure 2). New Re-Os molybdenite ages are presented here to constrain the age of these mineral occurrences in the Northern Patagonian Andes, and its relation with the magmatism of the North Patagonian Batholith.

Re-Os IN MOLYBDENITES

One fundamental question in metallogenesis is the age of the mineralization events associated with a mineral deposit. This matter is generally addressed by indirectly dating silicates associated to the mineralization, using methods such as the K-Ar, Ar/Ar and U-Pb isotopic systems. These systems are used to determine the age of the hydrothermal alteration (K-Ar, Ar/Ar) or the age of crystallization (U-Pb) of the intrusions that host the mineralization. On the other hand, the Re-Os isotopic system has demonstrated to be a reliable geochronological tool in the determination of the age of mineral deposits (McCandless *et al.*, 1993; Stein *et al.*, 2001, Barra and Ruiz, 2003) by direct determination of the age of sulfide phases.

The molybdenite mineral constitutes a particular case within the Re-Os system because it contains little or virtually no initial Os (common osmium), but contains high concentrations of Re (tens to hundreds of ppm) and ^{187}Os (ppb); the latter produced by the radioactive decay of ^{187}Re. Hence, the general equation of radioactive decay for the Re-Os isotopic system (equation 1) is simplified for molybdenite (equation 2):

$$(^{187}Os/^{188}Os)_{today} = (^{187}Os/^{188}Os)_{initial} + (^{187}Re/^{188}Os)_{today} (e^{\lambda t} - 1) \qquad (1);$$

$$[^{187}Os]_{today} = [^{187}Re]_{today} (e^{\lambda t} - 1) \qquad\qquad (2);$$

Thus, considering a decay constant (λ) of 1,666 x 10^{-11} a^{-1} (Smoliar *et al.*, 1996), the age can be calculated using the following expression:

$t = \ln [(^{187}Os/^{187}Re) + 1] / 1,666 \times 10^{-11}$.

Although the Re-Os system applied to molybdenites has proven to be a reliable dating tool, there is still controversy regarding the possible post-depositional disturbance of the Re-Os isotopic system (McCandless *et al.*, 1993; Suzuki *et al.*, 2000; Barra and Ruiz, 2003). To better determine if the ages obtained reflect a mineralization age or a disturbed age it is recommended to perform replicate analyses of samples or to compare the Re-Os ages with ages obtained by other systems (K-Ar, Ar/Ar or U-Pb) or by Re-Os age determinations of different co-genetic samples.

MOLYBDENITES OCURRENCES AND Re-Os RESULTS

Two localities with molybdenite occurrences have been reported in the area of study (SERNAGEOMIN-BRGM, 1995; Duhart *et al.*, 2000): at the Reloncaví Estuary and near the Palena village (Figures 1 and 2).

Near the Palena village, molybdenite occurs associated with Cretaceous monzogranites, and the mineralization consists of an assemblage of pyrite (partially oxidized)-chalcopyrite-molybdenite. Molybdenite appears as sparse disseminations in leafy heaps of up to 5 mm in the host rock and preferably in quartz rich zones (aplitic and pegmatitic dykes). Two samples of molybdenite were separated (PD-0017 and PD-0080) and dated by Re-Os techniques (Table 1). Sample PD-0017 was replicated to improve the reliability of the age (Table 1).

Table 1: Re-Os ages for molybdenite from Palena and Reloncavi Estuary. The uncertainty in the age determination is calculated using error propagation, considering weighing errors, analytical errors, the uncertainty in the Re decay constant (0.31 %) and uncertainties in the ^{185}Re and ^{190}Os spikes calibrations (0.08 and 0.15 %, respectively). Uncertainties for ages are absolutes (2σ).

Location	Sample	Type	Weight (mg)	Total Re (ppm)	^{187}Re (ppm)	^{187}Os (ppb)	Re-Os age (Ma)
Palena	PD-0017 (1)	disseminated	54	44,5	28,0	55,9	119.6 ± 0.6
Palena	PD-0017 (2)	disseminated	61	52,4	32,9	64,9	119.2 ± 0.6
Palena	PD-0080	disseminated	32	22,2	13,9	29,7	127.4 ± 0.6
Reloncaví Estuary	PD-0073	vein	66	83,8	52,7	8,1	9.09 ± 0.05
Reloncaví Estuary	PD-0073R	vein	82	178,5	112,2	17,1	9.13 ± 0.05
Reloncaví Estuary	PD-0075A (1)	vein	88	146	91,8	12,6	8.21 ± 0.04
Reloncaví Estuary	PD-0075A (2)	Vein	80	65,4	41,1	5,7	8.25 ± 0.04

In the Reloncaví Estuary, mineralization consists of pyrite-chalcopyrite-molybdenite associated to a Miocene biotite-tonalite intrusion. Molybdenite appears mainly in thick (3-10 cm) quartz veins as leafy radial aggregates and scarcely as small disseminations. In some cases, the veins are in sharp contact with the host rock, whereas in other cases the contacts are gradual. Three samples of molybdenite were separated (PD-0073, PD-0073R y PD-0075A) and dated (Table 1). One of them (PD-0075A) was replicated in order to determine if the difference of age between the two samples was due to different events or possible post-depositional disturbance of the Re-Os system (Table 1).

CONCLUSIONS

In the Palena village, field observations indicate that the molybdenite mineralization is closely related to the monzogranitic intrusion, and that the mineralization is possibly associated to a late magmatic event. Two different Re-Os ages (119 and 127 Ma) were obtained from two different samples within the same area. In order to determine if the ages obtained represent two different mineralization events or disturbed ages, a replicate analysis of sample PD-0017 was performed. The replicate analysis yielded the same age, within error, as the previous determination, attesting for the reliability of the age. Unfortunately, due to the limited amount of PD-0080 sample, no replicate analysis could be done on this sample. Although the reliability of the ~127 Ma age could not be assessed, the significant variation between the two Re-Os ages cannot be interpreted as the duration of a single hydrothermal event. Two alternatives can be evaluated in order to determine the significance of this older Re-Os age: (1) it might represent an older mineralization event or (2) the Re-Os system is disturbed in this sample. Previous K-Ar age determinations in the area (123±3 Ma K-Ar in biotite, 117±4 Ma K-Ar in hornblende and 116±3 Ma K-Ar in biotite; all ages at 2-sigma level) overlap within error with the ~119 Ma Re-Os age. This suggests that the ~127 Ma age represents a disturbed age rather than a possible older mineralization event. It has been stated that Re loss would yield older ages (McCandless et al., 1993), as may be the case here. Petrographic observations suggests that oxidation of pyrite and the consistent incorporation of iron oxides between molybdenite sheets maybe the cause of this disturbance by migration of Re into the iron oxides.

Field observations in the Reloncaví Estuary, i.e. the disseminated nature of the scarce mineralization, absence of widespread hydrothermal alteration and the gradual contact of some veins with the host rocks, indicate that the mineralization is also a late magmatic event, closely associated with the tonalitic stock. The Re-Os ages obtained (Table 1) indicate two mineralization events within a very short period of time (1 Ma): one at ~9.1 Ma and a younger event at ~8.2 Ma. The reliability of the determinations was assessed by replicate analysis of sample PD-0075A, and by analyses of two different co-genetic samples (PD-0073 and PD-0073R). Field evidence suggest that these two molybdenite events are the result of a single hydrothermal event that remained active for ~1 Ma, rather than two independent hydrothermal episodes.

The younger episode (~8.2 Ma) barely overlaps with a K-Ar age of biotite of 7.8±0.4 Ma (SERNAGEOMIN-BRGM, 1995) from the mineralized tonalitic intrusion. The Ar blocking temperature in biotite (300±50 °C) indicates that the system reached this temperature at *ca.* 7.8 Ma. This fact, coupled with the estimated closure temperature for the Re-Os system in molybdenite (>500 °C; Suzuki *et al.*, 1996), suggests a very fast cooling for the tonalite intrusion.

Complementary geochronological studies (U-Pb in zircons and Ar/Ar step heating in biotite), currently in progress, in samples from these same outcrops, will allow us to better constrain the age of crystallization and the cooling history of the granites associated with the mineralization. These new isotopic data with the Re-Os molybdenite ages presented here, will result in a better understanding of the evolution of the magmatic-mineralization systems in this region.

Figure 1: Image TM-741 showing the main geomorphologic units in the Northern Patagonian Andes, study area and location of molybdenite occurrences.

LEGEND

Deposits and volcanic and sedimentary rocks

☐ Fluvial, glacifluvial and glacial deposits, Quaternary

▨ Pyroclastic deposits and volcanic rocks, Quaternary

▨ Volcano-sedimentary deposits, Quaternary

▨ Sedimentary rocks, Tertiary

▨ Volcanic rocks, Tertiary

▨ Volcanic and sedimentary rocks, Jurassic-Cretaceous

■ Sedimentary rocks, Triassic

Plutonic and hypabisal rocks

▨ Granitic rocks and dacitic hypabisal, Eocene

▨ Granitic rocks, North Patagonian Batholith, Meso-Cenozoic

▨ Granitic rocks, Paleozoic

Metamorphic rocks

▨ Bahia Mansa Metamorphic Complex, Paleozoic-Triassic

▨ Los Chonos Metamorphic Complex, Triassic-Jurassic

■ Cordillerano Metamorphic Complex, Paleozoic

O Vulcano

▨ Liquiñe-Ofqui fault zone

✱ Molybdenite occurrences

Figure 2: Geologic map of the chilean Andes between 41-44° S showing metallogenic belts in the Northern Patagonian Andes.
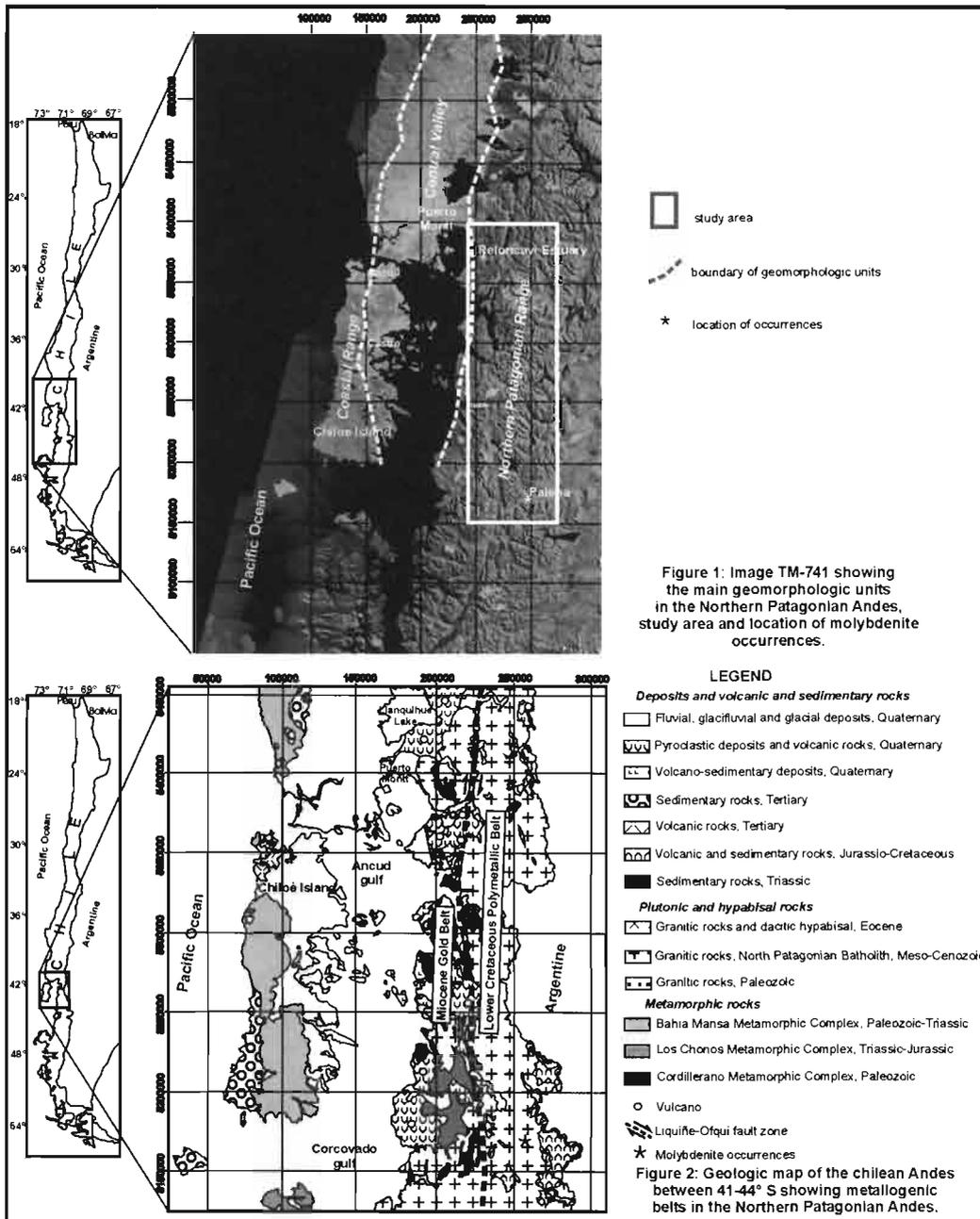
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