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Article

Age of the Angulos W-Mo mineralization from the Paimán Range (NW Argentina) and its geological significance

Fernando Guillermo Sardi and Holly Stein

With 2 figures and 2 tables

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Abstract: The hydrothermal W-Mo mineralization at Angulos in NW Argentina is genetically associated with the Potrerillos Granite, which is the host rock of the deposit. Re-Os dating of two molybdenite samples from the Angulos deposit yield mineral ages of 469.9 ± 1.6 and 464.8 ± 1.6 Ma (Middle Ordovician). The results are considered as the age of both hydrothermal mineralization and of the Potrerillos Granite which is part of the voluminous regional magmatism developed in the Famatina System. However, they are not in concordance with a previous Rb-Sr age of ~380 Ma for the Potrerillos Granite.

Key words: Re-Os, molybdenite, W-Mo deposit, Famatina System, NW Argentina.

Introduction

The Famatina System is a structural-geological province in northwestern Argentina. It has a main N-S orientation with a length of 340 km and a width of about 60 km. The Famatina System is located in the central-south and central regions of the Catamarca and La Rioja provinces and is surrounded by the Sierras Pampeanas geological province. An abundance of granitic rocks is a common feature of both geological provinces, with the main difference being the presence of Ordovician volcanic-sedimentary rocks in the Famatina System.

Molybdenite is present in different types of deposits within the Famatina System and the Sierras Pampeanas. It is found in high temperature hydrothermal W-Sn deposits, usually with vein quartz and stockwork morphologies, and genetically associated with felsic and evolved granites of Paleozoic age (e.g. Sardi et al. 2005; Ávila 2004; Ávila et al. 1999). These deposits are small in size and lack economic interest. Molybdenite can also be found in Cu-porphyry deposits which are genetically related to Tertiary volcanism of the Andean Orogeny. As opposed to the Paleozoic deposits, these deposits are of economic interest.

Molybdenite is a useful mineral for dating since it almost contains high concentrations of Re, whose radioactive ^{187}Re isotope decays to ^{187}Os. Furthermore, the ^{187}Os present in molybdenite is only of radiogenic origin since it does not take in any initial Os for crystal-chemical reasons (Stein et al. 2001, 2003). The Re-Os system provides the age of molybdenite crystallization and remains unaffected by metamorphic events (Stein & Bingen 2002; Stein 2006), even at granulite facies conditions (Bingen & Stein 2003; Bingen et al. 2006).

In Argentina, the method has been used by Garrido et al. (2008) to obtain the mineralization age of the La Voluntad Cu-Mo porphyry deposit in Neuquén

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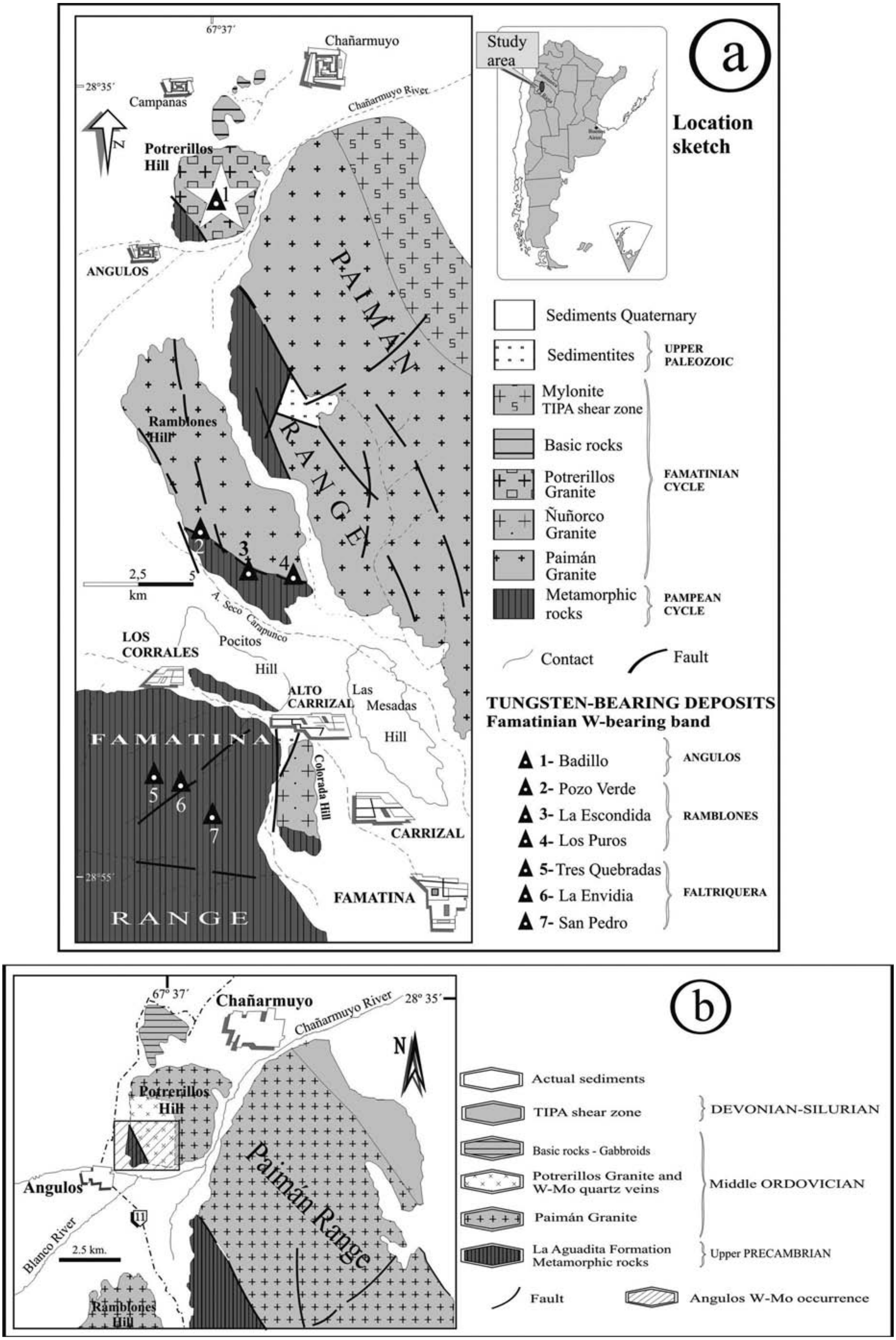

Fig. 1. a. General map of the center-east of the Famatina System. b. Local map of the W-Mo Angulos deposit.

province (SW Argentina) yielding a Carboniferous age. Also, Bierlein et al. (2006) have determined a Re-Os age of ~440 Ma for arsenopyrite and pyrite from Au-bearing quartz veins of the Sierra de Rinconada (Puna, NW Argentina).

The Angulos W-Mo deposit is located in the NE sector of the Pamián range (Famatina System, NW Argentina), and it is known as the 'Badillo' mine by the villagers. It is a very small deposit exploited for tungsten minerals during the beginning and middle of the last century using rudimentary methods without sophisticated mechanization; data on the production is imprecise. In this contribution, the Re-Os age of molybdenite from the Angulos W-Mo deposit is presented; additionally, local and regional implications are discussed.

Regional geology

Two prominent orogenic events are recognized in northwestern Argentina during the Upper Precambrian – Lower and Middle Paleozoic. These are the Pampean and the Famatinian orogenic cycles. The first cycle spanned the Upper Precambrian – Lower Ordovician and is characterized mainly by predominantly clastic sedimentation in a marine basin developed in NW Argentina along the passive margin of the Gondwana craton. The upper limit of the Pampean cycle is defined by paleontological studies of preserved marine fossils (Verdecchia et al. 2007).

The Famatinian cycle spanned the Middle Ordovician – Lower Carboniferous and is characterized by voluminous granitic intrusions and regional and dynamic metamorphism (e.g., Pankhurst et al. 2000; Rapela et al. 2001a and b; Höckenreiner et al. 2003; Miller & Söllner 2005).

Famatina System

The basement of the Famatina System consists of meta-sedimentary rocks (pelites and psammites) originated during the Pampean cycle. They were grouped as the Negro Peinado Formation by Turner (1960), but the same rocks, with fossil traces, are known as the La Aguadita Formation (Durand & Aceñolaza 1990).

An important volume of granitoids intruded the basement rocks during the Early and Middle Ordovician, corresponding to the Famatinian cycle (Miller & Söllner 2005). The magmatism was related to an active magmatic arc ('the Famatina arc') on continental crust (Miller & Söllner 2005; Pankhurst et al. 1998). Several W deposits in the area originated from this felsic magmatism.

The Angulos W-Mo deposit is located in the eastern region of the Famatina System and in the northern part of the "Famatinian tungsten belt" defined by Sardi et al. (2005) (Fig. 1a). This belt consists of a series of N-S aligned W deposits located along the 67º 38´ W meridian. They are small non-economic deposits of W contained in quartz veins and lenses that are hosted in granitic and/or metamorphic rocks. They are genetically associated with Lower to Middle Ordovician granitoids (Loske & Miller 1996; Rapela et al. 1999; Pankhurst et al. 2000; Varela et al. 2008).

Local geology

Paimán Range

The Paimán Range is composed essentially of granitic and mafic igneous rocks belonging to the Famatinian cycle and scarce outcrops of metamorphic basement rocks belonging to the Pampean cycle. Most of the range is occupied by the porphyritic Paimán Granite. It is characterized by idiomorphic K-feldspar megacrysts up to 15 cm in length, plagioclase and quartz, with biotite and muscovite as main accessory minerals. The Campanas Granite outcrops in the northwestern part of the Paimán range. It is a coarse-grained equigranular, biotite- and hornblende-bearing monzogranite. The contact with the Paimán Granite is gradational. The Campanas Granite contains zoned mafic intrusions of hornblende- and biotite-bearing gabbronorite, in the cores, grading outwards to diorite-tonalite (Pérez & Kawashita 1992) (Fig. 1). The continental sedimentary Agua Colorada Formation of Pennsylvanian age overlies the Paimán Granite.

The TIPA shear zone (López & Toselli 1993) is located between the Famatina System (to the west) and the Sierras Pampeanas (to the east) and affects the Paimán Granite on the eastern part of the range (Fig. 1) producing mylonitic rocks. This regional deformation event represents the collision and amalgamation of the Famatina magmatic arc with the Pampean hinterland (Höckenreiner et al. 2003).

The Potrerillos Granite is the rock hosting the Angulos deposit. It is a leucogranite stock located in the northeastern part of the Paimán Range (Fig. 1b). The Potrerillos Granite has a tectonic contact (fault) with meta-pelite and meta-psammite rocks of the La Aguadita Formation.

The Potrerillos Granite is genetically related to the Angulos deposit (Sardi 2005a). The texture is medium-

Table 1. Re-Os data for molybdenites from the W-Mo Angulos deposit, La Rioja Province, Famatina System, NW Argentina.

AIRIE Run #	Sample	Description	Re, ppm	^{187}Os, ppb	Age, Ma
MDID-519	#5935	Disseminated molybdenite in massive quartz vein-lenses at contact with Potrerillos granite	11.27 (1)	55.66 (4)	469.9 ± 1.6
MDID-550	#5935	as above	2.377 (2)	11.62 (1)	464.8 ± 1.6

Assumed initial $^{187}Os/^{188}Os$ for age calculation = 0.2 ± 0.1
Common Os less than 0.3 ppb
Absolute uncertainties shown, all at 2-sigma level, for last digit indicated
Decay constant used for ^{187}Re is 1.666 x $10^{-11}yr^{-1}$ (Smoliar et al. 1996)
Carius tube dissolution using double Os spike on 50 mg (MDID-519) and 18 mg (MDID-550) separates
For MDID-519, Re blank = 16.55 ± 0.09 pg, total Os = 5.96 ± 0.04 pg, $^{187}Os/^{188}Os$ = 0.568 ± 0.004
For MDID-550, Re blank = 5.94 ± 0.06 pg, total Os = 1.208 ± 0.007 pg, $^{187}Os/^{188}Os$ = 0.456 ± 0.006
Ages calculated using $^{187}Os = ^{187}Re (e^{\lambda t} - 1)$, and reported errors include analytical and ^{187}Re decay constant uncertainties

grained equigranular and the composition varies from granodioritic to syenogranitic with accessory minerals such as micas (biotite and muscovite), fluorite, allanite, wolframite and rutile (Sardi 2005 a and b).

Angulos deposit

The orebodies in the Angulos deposit are comprised mainly of small quartz veins and lenses in the cupola of the Potrerillos Granite. Secondary muscovite occurs as prominent alteration in the granite and is often associated with the mineralization. Also, incipient Na-metasomatism affects the microcline of the granite. Fractionation of metals into residual magmatic and hydrothermal phases, enriched in volatile components (F among them), and fracturing of the cupola of the granite allowing emplacement of quartz-veins, are considered the most important genetic factors (Sardi 2005a).

Molybdenite is the main sulphide present in the Angulos W-Mo deposit. It is a primary mineral together with other minerals such as wolframite, scheelite, cassiterite and pyrite (Sardi 2005a). The molybdenite is homogeneous regarding its physical appearance and size; it appears commonly as thin sheets with diameters of around 1 cm. It has a silver gray color, with a slight bluish tint.

Results

Sample 5935 contains fragments from the quartz-vein at the Angulos deposit. Well-formed crystals of molybdenite are characteristic. The sample was taken from the mine dump. The geographic coordinates are 28º38'4.8" S / 67º38'25.2" W. Two molybdenite crystals were analyzed under the AIRIE Program at Colorado State University, USA) and yield Re-Os mineral ages of 469.9 ± 1.6 and 464.8 ± 1.6 Ma (Table 1). Detailed analytical procedures are found in Zimmerman et al. (2009) and are summarized in the footnotes in the Re-Os data table.

As the ages obtained are slightly dissimilar, the molybdenites from the Angulos deposit could have formed in different mineralization stages or more likely over a period of several million years. The Re content is 11.3 ppm for the 'earliest' molybdenite and 2.4 ppm for the 'latest' one. Fitting with our interpretation, Sardi (2005b) suggested multistage mineralization for the formation of the ore-minerals in the Angulos deposit based on large compositional variation of the wolframites.

Discussion

Previous geochronological studies on rocks of the Paimán range

Durand & Aceñolaza (1990) studied soft body impressions – *Paliella* – and ichnogenus – *Planolites* – in meta-pelites and meta-psammites of the La Aguadita Formation outcropping in the Paimán Range that indicate an Upper Precambrian-Lower Cambrian age for the protholithic marine sediments. On the other hand, a K-Ar geochronological study by Collo et al. (2008) established the age of metamorphism as 'early' Lower Silurian (435 Ma for the La Aguadita Formation).

Magmatism in the Paimán Range is represented mainly by the Paimán, Campanas and Potrerillos granites. The former is the main unit and has been

Table 2. Summary of the relative and absolute ages for main Paleozoic lithological units of the Paimán Range, Famatina System. Previous works and data of this report.

Unit	Rock Type	Methods And Materials	Age (Ma)	Reference
La Aguadita Formation	Metapelites and metapsammites	Paleontological and biostratigraphic studies	Upper Precambric – Lower Cambrian (sedimentation)	DURAND & ACEÑOLAZA (1990)
		K-Ar (fine grained)	Early Lower Silurian (metamorphism)	COLLO et al. (2008)
Paimán Granite	Porphyritic granite	K-Ar on biotite	440-407 (± ~12)[1] (magmatism)	MCBRIDE et al. (1976)
		K-Ar on biotite	470-430 (± ~12) 347- 310[2] (± ~12) (magmatism)	GONZÁLEZ et al. (1985 a, b)
		K-Ar on biotite	454-437 (± ~13) (magmatism)	PÉREZ & KAWASHITA (1992)
		Rb-Sr on whole rock	499 (reference isochron) (magmatism)	PÉREZ & KAWASHITA (1992)
		U-Pb on zircon	477.6 ± 4.1 (magmatism)	VARELA et al. (2008)
Campanas Granite	a) Granitoids and b) ZMI[3]	Rb-Sr on whole rock	499 (reference isochron) (magmatism)	PÉREZ & KAWASHITA (1992)
		K-Ar on biotite	459 ± 24 (magmatism)	PÉREZ & KAWASHITA (1992)
		Rb-Sr on whole rock	459 ± 29 (magmatism)	PÉREZ & KAWASHITA (1992)
Potrerillos Granite	Granodiorite, monzo-syenogranite	Rb-Sr on whole rock	379 ± 15 (reference isochron) (magmatism)	PÉREZ & KAWASHITA (1992)
Angulos W-Mo deposit	Quartz veins	Re-Os on molybdenite	469.9 ± 1.6 464.8 ± 1.6 (mineralization)	This report
TIPA belt	Mylonites, orto-gneiss	Sm-Nd on garnet[4]	402.0 ± 2.0 (mylonitization)	HÖCKENREINER et al. (2003)
Agua Colorada Formation	Psamites and pelites	Paleontological data	Upper Carboniferous (sedimentation)	DURAND & ACEÑOLAZA (1990)

[1] the error in absolute ages is averaged; [2] these results are the samples that come from the east part of Paimán Range which has had an intense deformation; [3] ZMI: zoned mafic intrusions (PÉREZ & KAWASHITA 1992); [4] the sample don't came from Paimán Range but rather from near localities located in the north of the Paimán Range (Copacabana range).

dated by several authors. MCBRIDE et al. (1976) obtained ages between 407 and 440 Ma using the K-Ar method on biotite. GONZÁLEZ et al. (1985 a and b) obtained a wide range of ages between 310 and 470 Ma also using the K-Ar method on biotite. It should be noted that the younger ages are from the eastern flank of the Paimán Range, where an intense dynamic metamorphic event (the TIPA shear zone) affected the Paimán Granite. Therefore, these ages are probably not crystallization ages but rather disturbances associated with the deformational event. Recently, VARELA et al. (2008) obtained an age for the Paimán Granite of 477.6 ± 4.1 Ma using the U-Pb on zircon method, which was interpreted as the crystallization age.

PÉREZ & KAWASHITA (1992) applied K-Ar and Rb-Sr methods to obtain ages for different igneous rocks of the Paimán Range. K-Ar on undeformed biotite from the Paimán Granite yielded ages between 437 and 454 Ma, while a "reference isochron" (Rb-Sr on whole rock) yielded 499 Ma. This last age is also considered the age of the Campanas Granite because both granites appear to be contemporaneous. In addition, these authors obtained ages of 459 Ma from both K-Ar on amphibole and Rb-Sr isochron dating for zoned mafic intrusions.

The Potrerillos Granite represents the last magmatic event in the study area and has a well-known genetic link with the Angulos W-Mo deposit (Sardi 2005a). Pérez & Kawashita (1992) dated this granite using Rb-Sr on four whole rock samples. The re-calculated isochron yields an age of 379 ± 15 Ma with an initial ratio of 0.71 ± 0.08. This age is considerably younger than the Re-Os ages we have obtained for the molybdenites from the Angulos deposit. The younger age obtained by Pérez & Kawashita (1992) probably does not correspond to the crystallization age of the Potrerillos Granite, but reflects post-crystallization disturbance of the Rb-Sr system.

Höckenreiner et al. (2003) carried out a detailed geochronological study of the TIPA shear zone in localities located in north of the Paimán Range. The crystallization age of the protolith granitoid affected by the TIPA shear zone is 487.5 ± 3.6 Ma (U-Pb on zircon), while the main age attributed to deformation is 402.0 ± 2.0 Ma (Sm-Nd on syn-kinematic garnet).

The sedimentary rocks of the Agua Colorada Formation overlie the Paimán Granite in the southern part of the study area. They are not deformed and contain micro flora that are distinctly of Pennsylvanian age (Durand et al. 1990). Table 2 summarizes the temporal distribution of the main Paleozoic units in the study area and surrounding regions, presenting both absolute and relative ages.

Regional implications

The ages obtained in this paper indicate that the W-Mo mineralization in the study area is coeval with abundant magmatism dated by U-Pb for several granitoids in neighboring locations of the Famatina System (Loske & Miller 1996; Pankhurst et al. 2000; Dahlquist et al. 2005; Varela et al. 2008) and the Sierras Pampeanas (Pankhurst et al. 2000; Báez et al. 2008). The U-Pb zircon ages determined by these authors for granitic units surrounding the study area, such as those in the Famatina, Velasco and Mazán ranges, fall in the interval 463-484 Ma. Thus, emplacement of these Ordovician magmas, in some cases was accompanied by hydrothermal fluids, constrained to the Lower-Middle Ordovician interval. Toselli et al. (2002) has proposed an active arc setting at this time. Other radiometric methods, such as K-Ar on biotite and Rb-Sr (micas and whole rock) previously used by McBride et al. (1976), González et al. (1985a; 1985b) and Pérez & Kawashita (1992) on the Paimán Granite, are consistent with this time interval.

Nevertheless, a younger magmatism generated under an extensional post-orogenic setting intruded the deformed Ordovician granitoids (Toselli et al. 2006), and is recorded in the Velasco and Fiambalá ranges, east and north of the Paimán Range respectively (Fig. 2). This Carboniferous magmatism produced fertile and evolved granites with different ore-mineral assemblages. Grosse et al. (2009) determined crystallization ages of 344-358 Ma using U-Pb on zircon and monazite for granites located in the central-eastern zone of the Velasco Range, which contains both Be and W mineralization. The tin-bearing San Blas Granite, located in the northern part of the Velasco Range was dated by Báez et al. (2004) and Dahlquist et al. (2006) at 334 ± 5 Ma (U-Pb on zircon) and 340 ± 3 Ma (U-Pb SHRIMP), respectively. Finally, Sn±W and W±Sn deposits, usually vein-type, and associated with Carboniferous post-orogenic granites can also be found in the Fiambalá and Mazán ranges and Cerro Negro (Fogliata et al. 2012).

The Re-Os molybdenite ages of the Angulos deposit show that the W-Mo mineralization occurred in the Middle Ordovician. Moreover, the obtained molybdenite ages are the first geochronologic data obtained directly on the mineralization from a deposit from the 'Famatinian tungsten belt' of Sardi et al. (2005), confirming the Ordovician age of this belt.

Conclusion

The Angulos W-Mo deposit (Paimán Range, Famatina System, Argentina) is genetically related to the Potrerillos Granite and both wolframite and molybdenite are important ore minerals. Precise Re-Os ages of 469.9 ± 1.6 and 464.8 ± 1.6 Ma for two molybdenites from the Angulos deposit demonstrate a Middle Ordovician age. These Re-Os ages provide the time of mineralization for the Angulos W-Mo deposit. The slight difference in the two ages and Re contents in the analyzed molybdenites suggests a multistage and extended period of mineralization. Based on the molybdenite dating, we suggest the previously reported

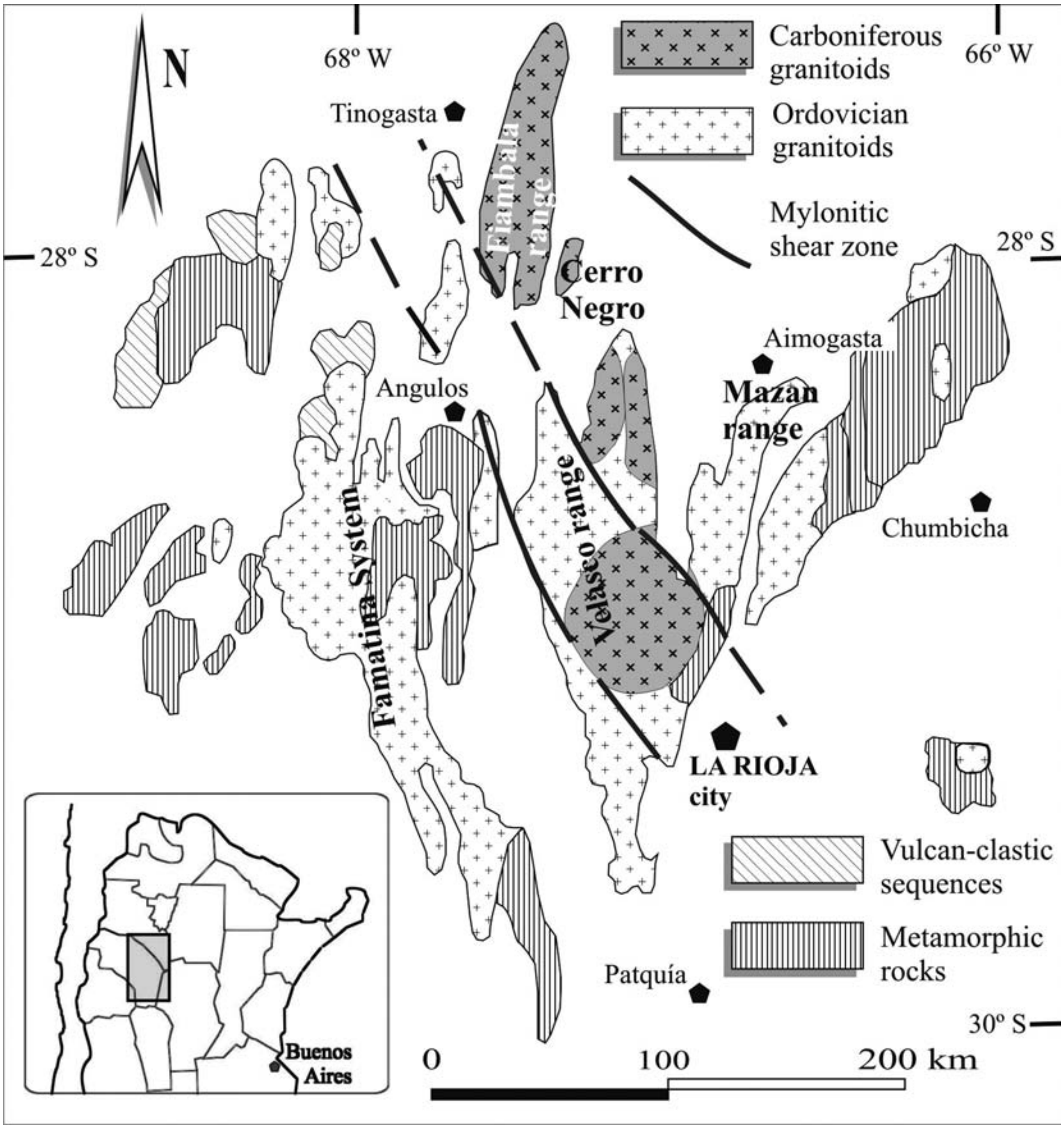

Fig. 2. Simplified geologic map of the Famatina System and closest neighbor Sierras Pampeanas showing the location of the main mineralized Carboniferous granitoids (see explanation on text).

age of 379 ± 15 Ma (Middle Devonian, whole rock Rb-Sr) for the Potrerillos Granite does not record the age of the Angulos deposit or the associated granite, but documents disturbed Rb-Sr isotope systematics. The disturbance likely originated from subsequent thermal events and fluid migration. The ages we report for the Angulos W-Mo deposit are consistent with other ages reported for Famatinian magmatism in surrounding regions.

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Address of the authors:

Fernando Guillermo Sardi, INSUGEO-CONICET, Miguel Lillo 205, 4000-San Miguel de Tucumán, Argentina.
e-mail: fgsardi@csnat.unt.edu.ar

Holly Stein, AIRIE Program, Department of Geosciences, Colorado State University, Fort Collins, 80523-1482 USA; Physics of Geological Processes, University of Oslo, 0316 Oslo, Norway.