Re-Os molybdenite and LA-ICPMS-MC U-Pb zircon geochronology for the Milpillas porphyry copper deposit: insights for the timing of mineralization in the Cananea District, Sonora, Mexico

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ABSTRACT

New geochronological data presented here improves the understanding of the temporal evolution of the Cananea Mining District, and particularly of the Milpillas porphyry copper deposit (northeastern Sonora, Mexico). Uranium-lead zircon analyses, using laser ablation ICP-MS multi-collector, from the quartz monzonite porphyry unit that host the mineralization at the Milpillas deposit, yielded a crystallization age of 63.9 ± 1.3 Ma (2-sigma). Re-Os molybdenite ages from two drill core samples from more than 500 m depth yielded an identical age of 63.1 ± 0.4 Ma (2-sigma), suggesting a restricted period of mineralization. These ages indicate that the Milpillas deposit is the oldest Laramide porphyry copper deposit recognized so far in the Cananea District. Our new Re-Os data in addition to previous Re-Os data, suggest that mineralization within the district, occurred within a ~4 m.y. period in three discrete pulses at ~59 Ma, ~61 Ma and ~63 Ma. This is in contrast to the previous model in which mineralization at the Cananea District was the result of a continuous hydrothermal system that started at ~62 Ma and ended at ~52 Ma.

Key words: U-Pb, Re-Os, geochronology, porphyry copper deposit, Laramide magmatism, Milpillas, Cananea, Mexico.

RESUMEN

Nuevos datos geocronológicos permiten un mejor entendimiento de la evolución temporal del Distrito Minero de Cananea y en particular del depósito de tipo pórfido cuprífero de Milpillas (noreste Sonora, México). Análisis de uranio-plomo en zircones, usando ICP-MS con multicolector y ablación por láser, del pórfido cuarzo monzonítico hospedante de la mineralización en el yacimiento de Milpillas, arroja una edad de 63.9 ± 1.3 Ma (2 sigma). Edades de Re-Os en molybdenita de dos muestras de núcleos de barrenación de más de 500 m de profundidad producen una edad idéntica de 63.1 ± 0.4 Ma (2 sigma). Esto sugiere un periodo de mineralización restringido. Estas edades indican que el depósito de Milpillas es el depósito Laramídico de tipo pórfido cuprífero más antiguo reconocido hasta el momento en el distrito de Cananea.
INTRODUCTION

The Southwest North America is one of the most important mineralized regions in the world. This metallogenic province is notable for copper, molybdenum, gold, silver and platinum resources (Titley, 1995). It contains more than 50 deposits, some of which are considered giant ore deposits; among them Morenci in the US, and Cananea and La Caridad in Mexico.

The first attempt to determine the timing of mineralization and magmatism of Mexican porphyry copper deposits (PCDs) was by Damon et al. (1983). Later, McCandless and Ruiz (1993) provided the first Re-Os molybdenite ages for PCDs in the US Southwest and northern Sonora, Mexico, and concluded that there were two periods of regional mineralization, at ~74–70 Ma and at 60–55 Ma. More recently, Barra et al. (in press) provided new Re-Os molybdenite ages for ten porphyry copper deposits from northern Mexico. Their data expands the Laramide mineralization event to 50 Ma, and suggests the idea that porphyry mineralization could also have occurred at ~64 Ma. The older period of mineralization (74–70 Ma) has not yet been recognized in Mexico.

In recent years, and with the advancement of geochronological analytical techniques, new studies have been performed in order to determine the timing of mineralization and the duration of hydrothermal systems in different porphyry copper provinces of the world, particularly in the Chilean province (Marsh et al., 1997; Ossandon et al., 2001; Bertens et al., 2003, Padilla-Garza, 2003; Masterman et al., 2004; Maksaev et al., 2004). In the North American Southwest porphyry copper province advances have been made in only a few deposits (i.e., Sierrita, Jensen, 1998; Herrmann, 2001; Morenci, Enders, 2000; Bagdad, Barra et al., 2003; La Caridad, Valencia et al., 2005). However, at the district level the timing of the different deposits is generally not well constrained (i.e., Cananea District in Sonora, Mexico and Pima District in Arizona, USA).

The Cananea District, located in northeast Sonora, Mexico (Figure 1), has produced more than 3.5 million tons of copper (Pérez-Segura, 2001; written communication). This district is characterized by a cluster of deposits that includes the world class porphyry copper deposit of Cananea, Lucy and Maria mines, Milpillas and Mariquita projects and Los Alisos, El Toro, El Alacran and La Piedra prospects (Figure 2). These deposits have reserves of over 11 million tons of copper (Long, 1995).

In spite of the economic importance of the Cananea District, limited geochronological work has been done on the timing of mineralization and magmatism (Anderson and Silver, 1977; Damon et al., 1983; McCandless and Ruiz, 1993; Wodzicki, 1995; Carreón-Pallares, 2002). An important remaining question is whether the multiple centers of mineralization in the district are the result of one episode or multiple short-lived episodes.

In this paper, we report data from the Milpillas deposit, which is the prime example of a hidden deposit in Mexico, and specifically in the Cananea porphyry copper district, which ranks among the three largest known porphyry copper districts in North America. Here we use U-Pb in zircons and Re-Os in molybdenite to constrain the timing of magmatism and molybdenite mineralization in the Milpillas deposit. We also compare the new data with previous Re-Os molybdenite ages from ore deposits in the same district (McCandless and Ruiz, 1993; Barra et al., in press). The question of the number of mineralization episodes in the district is relevant both to the metallogeny of the Southwest North America and to provide guidelines for the development of exploration programs.

REGIONAL GEOLOGICAL SETTING

The Cananea District lies on the southwestern edge of the North American craton (Campa and Coney, 1983; Sedlock et al., 1993) (Figure 1). The basement of the terrane is the Precambrian Pinal Schist (1.68 Ga), intruded by 1.41–1.48 Ga anorogenic granites (Silver et al., 1977; Anderson and Silver, 1981; Anderson and Bender, 1989). Paleozoic sedimentary rocks in Northeast Sonora (González-León, 1986; Stewart et al., 1990; Gehrels and Stewart, 1998; Blodgett et al., 2002) represent the southern extension of the Cordilleran miogeoclinal and platform sequences (Rangin, 1978; Campa and Coney, 1983; Stewart, 1988) and these rocks are represented in the district by the Bolsa (Cambrian), Abrigo (Cambrian), Martín (Devonian) and Escabrosa (Mississippian) Formations, and part of the Permian Naco Group (Meinert, 1982; Wodzicki, 1995, 2001).

Precambrian and Paleozoic rocks are overlain by Triassic-Jurassic volcanic rocks (in the Cananea District are the Elenita and Henrietta Formations; Valentine, 1936),
which are intruded by Jurassic plutonic rocks. These rocks are part of a continental magmatic arc that extends from California, USA to Durango, Mexico (Anderson and Silver, 1978; Tosdal et al., 1989; Jones et al., 1995). The Bisbee Group of Late Jurassic–Early Cretaceous age crops out northeast of the area, but it is absent in the Cananea region, suggesting that this area was a topographic high during the Mesozoic (McKee and Anderson, 1998). Plutonic and volcanic rocks of Late Cretaceous–Eocene age are widespread throughout southern Arizona, New Mexico and northern Sonora and were emplaced during the Laramide orogeny. Most of the porphyry copper deposits in southwest North America are associated with the Laramide orogeny (75–50 Ma, Shafiquallah et al., 1980). The geologic setting of these deposits has been discussed in detail by Titley (1981, 1982), Titley and Beane (1981), Titley and Anthony (1989), and Titley (2001).

After a period of quiescence of about ~20 m.y., caused by the westward migration of the magmatic arc (Coney and Reynolds, 1977; Damon et al., 1981; Damon et al., 1983), intensive magmatism occurred and is represented by extensive volcanic sequences of Oligocene age (30–25 Ma) (Shafiquallah et al., 1980; Damon et al., 1981; Roldán-Quintana, 1981). During the Miocene, mid-crustal extension and core-complex formation occurred in Sonora between 27–12 Ma (Gans, 1997) causing disruption and rotation of the Cananea District (Carreón-Pallares, 2002).

**LOCAL GEOLOGY**

Numerous authors have described the geology of the Cananea District since the early 20th century (i.e., Emmons, 1910; Valentine, 1936). More recently, studies have focused on the geology of individual deposits that form part of the district (i.e., Perry, 1961; Ochoa-Landín and Echavarri, 1978; Meinert, 1982; Bushnell, 1988; Wodzicki, 1995; 2001; Carreón-Pallares 2002). de la Garza et al. (2003) performed the first descriptive work on Milpillas. This ore deposit is located in a zone of extension, common in the Basin and Range province, which is referred as the Cuitaca Graben (Figure 2).

![Figure 1. Location of the Cananae Mining District (open square) and other porphyry copper deposit (open circles); dashed lines are terrane boundaries (Campana and Coney, 1983; Sedlock et al. 1993).](image-url)
The Milpillas deposit located in the northern part of the Cananea District, is included within the down-dropped block 7 km wide Cuitaca Graben, which cuts the Cananea region from north to south (Figure 2). The eastern portion of the graben is at a shallower level than the western portion and is dominated by Tertiary gravels, Quaternary alluvium, and erratic outcrops of Laramide volcanic units. The deeper western part of the Cuitaca Graben is dominated by Quaternary alluvium. Close to the eastern boundary of the Cuitaca Graben, a small horst is present where scarce altered and oxidized outcropping reveals the existence of the Milpillas ore deposit (Figure 2).

The oldest rock unit that crops out in the Cananea District (Figure 2 and 3). This unit represents the basement for the region and has been dated at 1440 ± 15 Ma by U-Pb in zircon (Anderson and Silver, 1977). The Cananea Granite is overlain by a Lower Paleozoic platform sequence (Figure 3), mostly quartzite and carbonates, succeeded by the conformably overlying Upper Paleozoic carbonates of the Naco Group (Meinert, 1982). All these rock units crop out extensively at the Cananea mine area and its vicinity; however, neither units have been recognized in the Milpillas area (Figure 4), but may well be present at a greater depth than the current drill-core exploration program.

The lowermost unit from the volcanic stratigraphy that crop out in the Cananea District (Figure 3) is the Late Triassic – Early Jurassic Elenita Formation (Valentine, 1936), which consists of a sequence of volcaniclastic and sedimentary rocks that include rhyolitic flows and tuffs, interbedded with andesites, sandstones, quartzites and conglomerates. This unit can be correlated with the Mount Wrightson and Fresnal Canyon Formations from southern Arizona, which have been dated between 220 and 192 Ma (Tosdal et al., 1989).

In the Milpillas area, one the main volcaniclastic host
rock units is the Laramide Mesa Formation (Valentine, 1936), which unconformably overlies the Henrietta Formation (Figure 5). The Mesa Formation is a calc-alkaline volcaniclastic unit that has an average thickness of ~1500 m, and extensively outcrops throughout the Cananea District where it has been dated at ~69 Ma (Wodzicki, 1995). These volcanic rocks have a medium to high potassium content and consist of trachybasaltic to andesitic agglomerates, flows and tuffs, including dacite and trachydacite, with andesitic composition being dominant throughout the sequence. In the Cananea District, this unit commonly includes significant thicknesses of interbedded volcanic sandstones and agglomerates, as well as a unit of basaltic flows, synvolcanic diabase sills and domes, locally known as the Mariquita Formation (Valentine, 1936). The oldest volcanic unit that crops out at Milpillas belongs to the Jurassic Henrietta Formation (Valentine, 1936). This is a volcaniclastic sequence, which consists of calc-alkaline dacitic and rhyolitic flows and tuffs, interbedded with agglomerates, latites and andesites (Wodzicki, 2001). In the Cananea region, this unit overlies the Elenita Formation (Figure 3). The Henrietta Formation has been correlated with the Artesa sequence from southern Arizona (Tosdal et al., 1989). Although none of these units have been isotopically dated, a Mid- to Late Jurassic age (~165 to 150 Ma) has been assigned to them (Wodzicki, 2001).

Small porphyry stocks that vary in composition from quartz monzonite to monzonite intruded the Henrietta and Mesa Formations (Figure 3 and 5). The porphyry stocks consist of 2–5 mm quartz, feldspar and biotite phenocrysts in a matrix of aphanitic-fine quartz and orthoclase. The porphyry stocks are typically overprinted by strong sericitic alteration and are the main host to the Cu mineralization, but this Cu mineralization also extends into the immediate intruded volcaniclastic rocks. These porphyry stocks are spatially and could be genetically related to the late stages of the Laramide batholithic pluton complex locally known as the Cuitaca–Tinaja batholith. This plutonic unit outcrops extensively throughout the Cananea Mining District. The Cuitaca–Tinaja batholith is a granodiorite that contains biotite and hornblende as the main accessories, with minor magnetite and sphene. This pluton has been dated at 64 ± 3.0 Ma, using U-Pb in zircon (Anderson and Silver, 1977). No porphyry units crop out at the surface in the Milpillas area (Figure 5), however, there are some isolated outcrops of altered and leached volcanic host rocks. The ore body is completely covered by a sequence of post mineralization conglomerates and syntectonic gravels (Figures 2, 4, 5).

Figure 3. Generalized stratigraphic column for the Cananea District. Modified after Wodzicki (1995).
**Structural geology**

The structural control of PCDs emplacement in southwestern North America is consistent, at a district scale, with the dominant tectonic stresses that existed at their particular time of formation. These stresses vary from compressional to tensional (Titley, 2001). However, the tectonic evolution of this region has continued after ore deposit formation. During the relaxation of confining stresses at the North American–Pacific plate margin due to changes in plate motions and/or plate margin configuration in the mid- to late Tertiary (Gans and Miller, 1993; Basin and Range Province event), the region has been intensely faulted, extended and rotated, resulting in a significant disruption and rotation of deposits (e.g., San Manuel-Kalamazoo, Ajo, and Cananea). The magnitude of rotation varies from moderate (30° to 60°) to severe (60° to 90°) (Wilkins and Heidrick, 1995).

In the Milpillas area, three main lineaments have been described: a pre-mineral N-S trend, a syn-mineral NE trend, and a post-mineral NW trend (de la Garza et al., 2003). However, a detailed structural study of the Milpillas deposit from quartz veins and mineralized structures performed by Carreón-Pallares (2002) shows a flat radial and concentric structural pattern with preferential dips to the NE, E and SE. These dip trends are the same primary main orientations reported for Laramide stocks throughout Arizona (Rehrig and Heidrick, 1972; Heidrick and Titley, 1982), whereas the concentric pattern has been recognized in Sierrita, Arizona (Titley, 1982).

**Mineralization and alteration**

The hypogene mineralization in PCDs from the district is mainly present as breccias, stockwork and/or disseminated sulfide minerals. Where pre-Laramide sedimentary host rocks are present, skarn mineralization developed. High-grade, but low tonnage ore bodies, are found in skarn zones, as for example in the Cananea mine, where mineralization of Cu-Zn-Pb was developed by replacement of Paleozoic carbonate rocks interbedded with quartzites (Meinert, 1982). In some deposits, high grade mineralization was developed in breccias pipes, such as in the Cananea mine (Brecha La Colorado, Bushnell, 1988) or in Maria mine (Wodzicki, 1995). At the Milpillas deposit, scarce and low-grade hypogene or primary mineralization is recognized (0.15–0.20 % Cu) and because of these low grades, the exploration program focused on areas of supergene enrichment.

Most of the porphyry copper deposits in the Cananea
District have been dated by K-Ar dating techniques, yielding ages from \( \sim 60 \pm 4 \) Ma to \( \sim 54 \pm 2 \) Ma (Damon and Mauger, 1966; Damon et al., 1983; Wodzicki, 1995).

The Milpillas deposit is a secondary enriched porphyry copper deposit that consists of high-grade chalcocite blankets that are entirely covered by Tertiary–Quaternary alluvial sediments commonly 50–250 meters thick (de la Garza et al., 2003). Milpillas was discovered and developed after intensive exploration programs and more than 100,000 meters of drilling, initially by Minera Cuicuilco in 1975 and continued up to feasibility in 1998 by Industrias Peñoles mining company.

The supergene enrichment zone presents a vertical zoning with an upper leach cap and oxide level typical of porphyry copper systems. The secondary enriched zones (Figure 5) comprise the most important ore bodies in the deposit. These bodies can reach copper grades that range from >1% to more than 10%.

Descriptions of supergene mineralization are scarce or non-existing for Mexican PCDs. Seagart et al. (1974) provided the only known description of this type of mineralization in La Caridad. In the Milpillas ore body, the high grades of Cu are found in sub-horizontal bodies or blankets (Figure 5). At least three cycles of secondary enrichment are recognized in the deposit (see Anderson, 1982; Titley and Marozas, 1995; and Gilmour, 1995 for review of leach capping processes and supergene copper enrichment), which resulted in at least six ‘blankets’ that occur at a depth of 150 to 750 meters below the surface. The upper three blankets contain oxide mineralization and have a complex mineralogical assemblage consisting of: “green Cu-oxides-carbonates” (antlerite, brochantite, malachite, azurite and chrysocolla); “red Cu-oxides” (cuprite, native copper, delafossite, and minor “pitch” limonite); and “black Cu-oxides” (neotocite, melaconite, tenorite, and minor “Cu-wad”) (de la Garza et al., 2003). Below these three blankets is an intermediate horizon that contains a mixture of oxides and sulfides. The two deepest blankets contain dominantly secondary sulfide minerals (mainly chalcocite and minor covellite; de la Garza et al., 2003). Total copper resources for these blankets are 30 million tons at 2.5% Cu.

### ANALYTICAL PROCEDURES

#### Zircon U-Pb dating

A sample was collected from drill hole M-120 at a depth of \( \sim 540 \) m (Figure 5). The sample was crushed and milled. Heavy mineral concentrates of the <350 microns fraction were separated magnetically. Inclusion-free zircons from the non-magnetic fraction were handpicked under a binocular microscope. Zircons were mounted in epoxy and polished for laser ablation analysis.

Single zircon crystals were analyzed in polished sections with a Micromass Isoprobe ICP-MS multi-collector equipped with nine Faraday collectors, an axial Daly detector, and four ion-counting channels (Dickinson and Gehrels, 2003). The Isoprobe is equipped with an ArF Excimer laser, which has an emission wavelength of 193 nm. The analyses were conducted on 50–35 micron spots with output energy of \( \sim 32 \) mJ and a repetition rate of 10 Hz. Each analysis consisted of a background measurement (one 20-second integration on peaks with no laser firing).

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Figure 5. Cross section view of the Milpillas porphyry copper deposit. Also shown are sample locations.
and twenty 1-second integrations on peaks with the laser firing. Any Hg contribution to the $^{206}$Pb mass is accordingly removed by subtracting the backgrounds values. The depth of each ablation pit was ~20 microns. Total measurement time was ~90 s per analysis.

The collectors were configured for simultaneous measurement of $^{204}$Pb in an ion-counting channel and $^{206}$Pb, $^{207}$Pb, $^{208}$Pb, $^{232}$Th, and $^{238}$U in Faraday detectors. All analyses were conducted in static mode. Inter-element fractionation was monitored by analyzing fragments of SL-1, a large concordant zircon crystal from Sri Lanka with a known (ID-TIMS) age of 564 ± 4 Ma (2σ) (Gehrels, unpublished data). The reported ages for zircon grains are based entirely on the $^{206}$Pb/$^{238}$U ratios because errors of the $^{207}$Pb/$^{235}$U and $^{206}$Pb/$^{207}$Pb ratios are significantly greater. The larger errors are the result of the low intensity (commonly <0.5 mV) of the $^{206}$Pb signal from these young, low-U grains. $^{207}$Pb/$^{235}$U and $^{206}$Pb/$^{207}$Pb ratios and ages are accordingly not reported.

The $^{206}$Pb/$^{238}$U ratios are corrected for common Pb by using the measured $^{206}$Pb/$^{204}$Pb, a common Pb composition from Stacey and Kramers (1975), and an uncertainty of 1.0 unit on the common $^{206}$Pb/$^{204}$Pb.

The weighted mean of 16 individual analyses was calculated according to Ludwig (2003). The mean considers only the measurement or random errors (errors in $^{206}$Pb/$^{238}$U and $^{206}$Pb/$^{204}$Pb of each unknown). For this sample the random error is 0.6 Ma (2σ), and represents ~1%. Age of standard, calibration correction from standard, composition of common Pb, decay constant uncertainty are the other sources that contributed to the error in the final age determination. These uncertainties are grouped and are known as the systematic error. For this sample the systematic error is ~1.8%. The error in the age of the sample is calculated by adding quadratically the two components (random or measurement error and systematic error), which for this sample is ~2.1 % (i.e., 1.3 Ma). All age uncertainties are reported at the 2-sigma level (2σ).

**Molybdenite Re-Os dating**

Molybdenum mineralization at Milpillas occurs frequently intergrown with primary copper sulfides. In order to determine the timing of hydrothermal mineralization, two molybdenite samples where selected from two different drill holes M-120 (at ~540 m depth) and M-098 (at ~514 m depth) (Figure 5). Molybdenite sample M-120 was collected from a 4-mm-thick vein that has an assemblage of quartz-sericite-molybdenite and sample M-98 was collected from a 5-mm-thick vein with an assemblage of quartz-sericite-molybdenite-chalcopyrite-pyrite (Figure 6). Both samples are from the quartz monzonite porphyry unit, with a medium to strong quartz-sericite alteration (Figure 4) that overprints and partially replaces the original rock-forming silicates and their pre-existing alteration products (e.g., biotite and K-feldspar) (Beane, 1982).

The Re-Os system applied to molybdenite is an important tool in determining the timing of mineralization since ore minerals (molybdenite) are dated directly. Other dating techniques, such as K-Ar and Ar-Ar are applied to associated silicates and hence provide indirect age determinations. Furthermore, the very low errors obtained with the Re-Os technique (between 0.33% to <1% of age determination) allow us to constrain or identify different pulses of mineralization that may occur in very short periods of time (e.g., Maksaev et al., 2004). However, there is a continuous debate regarding the possible open-system behavior of Re and Os in molybdenite (see McCandless et al., 1993; Stein et al., 2001; Barra et al., 2003 for discussions).

Approximately 0.05 g of hand-picked molybdenite and spikes were loaded in a Carius tube with 8 mL frozen
reverse aqua regia. While the reagents, sample and spikes were frozen, the Carius tube was sealed and left to thaw at room temperature (Shirley and Walker, 1995). The tube was placed in an oven and heated to 240 °C for 12 hours. Osmium was separated from the solution in a two-stage distillation process (Nagler and Frei, 1997). Osmium was further purified using micro-distillation technique (Birck et al., 1997) and loaded on platinum filaments with Ba(OH)₂ for thermal ionization mass spectrometer (TIMS). After osmium separation, the remaining acid solution was dried and re-dissolved in 0.1 HNO₃. Rhenium was extracted and purified through a two-stage separation column using AG1-X8 (100–200 mesh) resin and loaded on nickel filaments with Ba(NO₃)₂ for TIMS measurements.

Samples were analyzed by negative thermal ion mass spectrometry (NTIMS) (Creaser et al., 1991) on a VG 54 mass spectrometer. Molybdenite ages were calculated using a ¹⁸⁷Re decay constant of 1.666·10⁻¹¹ year⁻¹ (Smoliar et al., 1996). Ages are reported with a conservative total error of 0.5 % (~2 sigma), which is a conservative approach that considers uncertainties from instrumental counting statistics, uncertainties in spike calibrations and in the ¹⁸⁷Re decay constant (0.31%). Blank levels are less than 7 ppt Os and 15 ppt Re.

Zircon U-Pb results

Sixteen zircon grains were measured from sample M-120. Results are reported in Table 1 and each line represents a spot analysis. All reported ages in Table 1 have uncertainties at the one-sigma level (1σ), which only includes the measurement error.

Zircons analyzed are clear pinkish in color and range from 80 to 250 μm in size. They are doubly-terminated prisms dominated by the [100] face with a 2.5–3:1 length to width ratio, which are typical morphologies of zircons in igneous rocks (Figure 7) Cathodoluminescence (CL) images show that the zircons have narrow zoning (Figure 7), which is characteristic of evolved magmas (Corfu et al., 2003). Measurements were made at the center and tips of zircon crystals.

Zircons from sample M-120 have U and Th concentrations that vary from 530–195 ppm and 240–88 ppm, yielding U/Th ratios of ~2, characteristic of igneous zircons (Rubatto, 2002). These zircons yielded a weighted average ²⁰⁶Pb/²³⁸U age of 63.9 ± 1.3 Ma (n=16, MSWD=0.91; Figure 8). In the sixteen grains analyzed, no older component was detected.

Molybdenite Re-Os results

Re-Os age determinations for two molybdenite samples are shown in Table 2. This table also includes previous data from the district reported by Barra et al. (in press).

Table 1. LA-ICPMS-MC U-Pb zircon data.

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</tr>
</tbody>
</table>

*All errors are at the 1-sigma level, and include only random uncertainties. For the sample age additional uncertainty from the calibration correction, decay constant and common lead was considered. These systematic errors (1.8 %) were added quadratically to the measurement error.

** ²⁰⁸Pb/²³⁸Pb is measured ratio.

Initial Pb composition interpreted from Stacey and Kramers (1975), with uncertainty of 1.0 for ²⁰⁸Pb/²³⁸Pb. Isotope ratios are corrected for Pb/U fractionation by comparison with standard zircon with an age of 564 ± 4 Ma (2-sigma). Decay constants: ²⁰⁶Pb=9.8485·10⁻¹⁰, ²³⁸U=1.55125·10⁻¹⁰, ²³⁸U/²³⁵U=137.88. U concentration and U/Th are calibrated by comparison with NBS SRM 610 and have uncertainty of ~25%.

DISCUSSION

Age of mineralization

The ²⁰⁶Pb/²³⁸U zircon age of 63.9 ± 1.3 Ma (Figure 8) for the mineralized quartz monzonite porphyry unit is the only crystallization age reported so far for a productive intrusion in the Cananea District. This age is similar to the Cuitaca Granodiorite (64 ± 3 Ma) that crops out in the western border of the Cuitaca Graben. However, this unit has not been identified in any of the several drill holes from the Milpillas area.

Molybdenite samples of two different mineral assemblages from two deep drill holes (separated about 100 m from each other), have identical Re-Os ages, suggesting that the molybdenite mineralization of Milpillas porphyry copper deposit occurred within a very short period of time (weighted average age of 63.1 ± 0.3 Ma).

Our U-Pb and Re-Os ages indicate a temporal relationship between the magmatism and hydrothermal activity, and identify the Milpillas porphyry copper deposit as the oldest Laramide porphyry in the Cananea District. Furthermore,
the limited data presented suggests that the duration of magmatic-hydrothermal activity in Milpillas was brief and that the hypogene mineralization was the product of a low-grade single complex intrusion as proposed by Gustafson (2000).

**Long-lived or short-lived multiple mineralization centers**

It is evident that knowledge of the age and duration of geologic events that result in the formation of important concentrations of ore minerals in the earth’s crust is fundamental to our understanding of the evolution and origin of ore deposits. For porphyry copper deposits, the long-lived magmatic-hydrothermal model versus the short-lived model, with several discrete pulses, and its role in the formation of large or giant ore deposits has become the focus of numerous recent studies (e.g., Arribas et al., 1995; Cornejo et al., 1997; Marsh et al., 1997; Clark et al., 1998; Hedenquist et al., 1998; Reynolds et al., 1998; Selby and Creaser, 2001; Barra et al., 2003; Mastermann et al., 2004; Maksaev et al., 2004). Consequently, the determination of the lifespan of porphyry copper systems and its relation with the size of the deposit (i.e., the amount of copper contained) is critical in the development of genetic models of PCDs at the deposit level and probably more relevant at the district level were porphyries tend to occur in clusters. Obviously, timing information is relevant in the construction of regional metallogenic models.

The pioneering work of Damon et al. (1983) remained for many years the only geochronological source on Mexican PCDs. This work reported several K-Ar ages of different K-rich minerals (i.e., hornblende, biotite, K-feldspar) for host rocks and mineralized porphyries. However, more recent age determinations using other techniques have shown that some of the K-Ar ages of Damon et al. (1983) do not represent the main hydrothermal-mineralization or magmatic episodes (i.e., El Arco Baja California, Mexico, K-Ar of ~98–106 Ma (Barthelmy, 1975) versus U-Pb and Re-Os of ~164 Ma (Valencia-Gómez, 2005); Cumobabi K-Ar of ~40 Ma compared to K-Ar of ~55.6–63.1 Ma (Scherkenbach et al., 1985) and Re-Os of ~59 Ma (Barra et al., in press). These K-Ar ages apparently record cooling rather than magmatic or hydrothermal events, and therefore led to erroneous metallogenic models of the region.

Figure 7. Cathodoluminescence photographs of zircons from sample M-120.
Porphyry copper deposits in the North America southwest did not form during temporally random or isolated events, but rather during the maturation of complex magmatic centers that progressed through a long-lived sequence of igneous episodes (Lang, 1991). The Cananea cluster, the largest porphyry Cu-Mo district in Mexico, is interpreted to be the result of long-lived magmatic-hydrothermal system, spanning from ~64 Ma to ~52 Ma (Figure 9, Meinert, 1982; Wodzicki, 1995). This statement was supported by the early span of time (>10 Ma) in the magmatic-hydrothermal system, which might be a function of disturbed Ar or a less precise Re-Os age.

Furthermore, it is possible that the large volume of metal in the Cananea mine is the result of overprinting of multiple discrete hydrothermal-mineralization events, in contrast to single mineralization events in María, Milpillas and El Alacrán. The limited geochronological data for Cananea does not allow us to test this hypothesis, however, several examples from Chilean porphyry copper deposits (i.e., Chuquicamata, Reynolds et al., 1998; Ballard et al., 2001; Ossandon et al., 2001; Los Pelambres, Bertens et al., 2003, La Escondida, Padilla-Garza et al., 2004; El Teniente, Maksaev et al., 2004) suggest that large deposits are the result of multiple overlapping of discrete mineralization episodes.

**Timing of mineralization in Northwest Mexico**

Porphyry copper mineralization in Northwest Mexico is Laramide in age (Damon et al., 1983), with the exception of El Arco in Baja California, which has an older Middle Jurassic age (164 Ma, Valencia-Gómez, 2005).

The Laramide orogeny is characterized in the North American southwest by a compressional regime with basement uplift and thrust fault deformation, and widespread igneous activity, which produced extensive calc-alkaline magmatism in southern Arizona, New Mexico, and Sonora ranging from 80 Ma to 40 Ma (Damon et al., 1964; Damon and Mauger, 1966; Coney, 1976; Shafigullah et al., 1980; Damon et al., 1983). McCandless and Ruiz (1993) determined two distinct intervals of porphyry copper mineralization in the southwestern region (including northern Mexico), one from 74–70 Ma and the other from 60–55 Ma, based on Re-Os systematics. However, in spite of this important and pioneering contribution, these ages were determined using less precise ICP-MS technique, and ages were calculated with the old Re-Os decay constant (1.64·10⁻¹¹ a⁻¹, Lindner et al., 1986), yielding results with high errors and slightly older ages. For example, the Re-Os molybdenite age of María mine calculated at 57.4 ± 1.6 Ma (1 sigma) is recalculated to 56.5 ± 3.2 Ma (2 sigma) using the latest Re-Os decay constant of 1.666·10⁻¹¹ a⁻¹ (Smoliar et al., 1996). This age is very close to the new Re-Os age determination from a sample from the same deposit using the more precise TIMS technique, which yielded an age of 60.4 ± 0.3 Ma (Barra et al., in press). This new determination and the small associated error, allow us to better constrain the relative timing of the different deposits in this important province.

Re-Os ages from a number of porphyry copper deposits in northwest Mexico: La Caridad (Valencia et al., 2005), El

<table>
<thead>
<tr>
<th>Location</th>
<th>Sample</th>
<th>Total Re (ppm)</th>
<th>⁸⁷⁸⁷Re (ppm)</th>
<th>⁸⁷⁸⁸Os (ppm)</th>
<th>Age (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milpillas</td>
<td>M-098</td>
<td>8785</td>
<td>5523</td>
<td>5805</td>
<td>63.1 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>M-120</td>
<td>6547</td>
<td>4116</td>
<td>4325</td>
<td>63.0 ± 0.4</td>
</tr>
<tr>
<td>El Alacrán*</td>
<td>B9</td>
<td>7352</td>
<td>4622</td>
<td>4690</td>
<td>60.9 ± 0.2</td>
</tr>
<tr>
<td>María*</td>
<td>MR1</td>
<td>316.9</td>
<td>199.2</td>
<td>200.4</td>
<td>60.4 ± 0.3</td>
</tr>
<tr>
<td>Cananea*</td>
<td>Incremento 3</td>
<td>95.7</td>
<td>60.2</td>
<td>59.5</td>
<td>59.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Brecha La Colorada</td>
<td>90.7</td>
<td>57.0</td>
<td>56.2</td>
<td>59.2 ± 0.3</td>
</tr>
</tbody>
</table>

* Data from Barra et al. (in press).

Molybdenite ages were calculated using a ¹⁸⁷Re decay constant of 1.666 · 10⁻¹¹ year⁻¹ (Smoliar et al., 1996). Ages are reported with a 0.5% error, which is considered a conservative estimate and includes the uncertainty in the Re decay constant (0.31%), ¹⁸⁷Re and ¹⁸⁷Os spike calibrations (0.08% and 0.15%, respectively), weighting and analytical errors.

Figure 8. U-Pb weight average plot from sample M-120.
Crestón, Cananea, El Alacrán, Suaqui Verde, María, and Cuatro Hermanos (Barra et al., in press), and Milpillas (this study), suggests that the two largest districts in northwest Mexico occurred in two intervals; at 63–59 Ma (Cananea District), and at 55–53 Ma (La Caridad District). Although mineralization in these districts formed in two different episodes, magmatism seems to have occurred over a much more extensive period, overlapping in space and time. This is illustrated in La Caridad, where 63.5 Ma volcanic rocks host the 54 Ma porphyry copper mineralization (Valencia et al., 2005). Similar examples of this have been recognized in other PCDs in the Arizonan province.

Finally, the ~70 Ma porphyry mineralization recognized in northern Arizona (e.g., Mineral Park, Titley, 1982; Bagdad, McCandless and Ruiz, 1993; Barra et al., 2003) has not yet been recognized in northwestern Mexico.

CONCLUSIONS

U-Pb zircon analyses from the mineralized quartz monzonite porphyry at the Milpillas deposit yielded a $^{206}\text{Pb} / ^{238}\text{U}$ age of $63.9 \pm 1.3$ Ma. This age coupled with molybdenite ages from two deep drill holes which have identical Re-Os ages (weighted average age of $63.1 \pm 0.3$ Ma), suggests that the mineralization of Milpillas porphyry copper deposit occurred within a short period of time.

Mineralization within the Cananea District occurred in...
at least three discrete periods, at ~59 Ma, ~61 Ma and ~63 Ma, supporting the model of multiple centers of mineralization produced by the short lived discrete periods rather than a long lived period of mineralization.

We suggest that the large volume of metal in the Cananea mine could result from the overprinting of multiple discrete periods of hydrothermal mineralization, contrasting with single mineralization event as in María, Milpillas and El Alarcón.

The largest mineralized districts in northwest Mexico occur in two main intervals, one at 59–63 Ma (Cananea), and the other at 53–55 Ma (La Caridad District), where associated magmatism overlaps in space and time.

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