Episodic magmatism and hydrothermal activity, Pima Mining District, Arizona

by

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Abstract

New U-Pb dating and a synthesis of previous geochronology improves understanding of the temporal evolution of the Pima Mining District, Arizona and particularly the Sierrita porphyry Cu-Mo system. Four of eight Laramide intrusions at the Sierrita deposit were dated with U-Pb methods. The new U-Pb ages describe the most accurate and precise magmatic history for the intrusive center.

The Pima district has a prolonged magmatic history with evidence for 15 m.y. of Laramide magmatic activity associated with several distinct hydrothermal episodes. The Sierrita porphyry system occurs at the southern end of the district and is centered on a series of porphyritic stocks. Field work, buttressed by K-Ar dating demonstrates that the earliest intrusive activity is represented by a quartz diorite and followed by a granodiorite batholith. Numerous porphyry plugs, breccias, and dikes complete the sequence. Mineralization is associated mainly with the earliest porphyry although to a smaller extent with others as well. Based on published, unpublished, and new U-Pb, K-Ar, and Re-Os dating, Laramide magmatic activity spanned 7-8 m.y. (68-60 Ma) in 3 discrete events (at 68-67, 64-63 and 60 Ma).

Ages of intrusion were compared with published thermal models to assess if the intrusive complex was the result of single or multiple magmatic episodes at the chamber scale, that is, if it was comagmatic. All intrusive activity at Sierrita is likely not comagmatic, but intrusions of singular, discrete events probably are. One ~3 m.y period of quiescence separates the main porphyry from smaller, later porphyries indicating that the total mineralization is the result of superimposed, separate, and discrete hydrothermal
systems. At least two other intrusive centers associated with the Ruby Star batholith have hydrothermal systems — the faulted Twin Buttes, Mission-Pima, San Xavier North center hosts major skarn mineralization in several fault blocks, whereas the older Red Boy center lacks known economic mineralization.
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Introduction

K-Ar geochronology at porphyry copper districts throughout the world suggests that the timing of mineralization at magmatic arcs may be restricted in time (Livingston et al., 1968; Sillitoe, 1988). This inference is based on the observation that the absolute ages of mineralization-related magmas and alteration at various deposits within a particular province appear to cluster around one or more discrete time intervals. These intervals are of significantly shorter duration than the arc. Proposed controls on such patterns are a deeper crustal filter effect that allows metals to reach economic concentrations in magmas in the lower crust, or a tectonic control related to changes in plate vectors that triggers the ascent of productive magmas into the upper crust (McCandless and Ruiz, 1993).

Examples of the apparent clustering of K-Ar ages are seen in the Chilean porphyry copper province at 66-52, 42-31, and 16-5 Ma (Sillitoe, 1988). In southwestern North America, Livingston et al. (1968; their figure 1) showed a clustering of K-Ar ages at 60-55 Ma for 15 plutons genetically related to porphyry mineralization. A recent study in the same province found that ages of molybdenite fell into two groups, from 74-70 Ma and 60-55 Ma (McCandless and Ruiz, 1993). The authors emphasized that the ages coincided regardless of the age of onset, duration, or magnitude of magmatism at each intrusive center. The implication is that mineralization is controlled by something beyond the scale of an individual magmatic system, which affects many separate systems.

Within an individual system, questions remain about the longevity of a system that produces a large ore deposit. Thermal models indicate that a short-lived system (up to
about 1 m.y.) could reflect formation by a single, continuous magmatic event at the magma chamber scale, whereas a long-lived system more likely represents multiple, episodic magmatic events (Norton and Knight, 1977; Cathles, 1981; Norton, 1982; Barton and Hanson, 1989). A current single-event model maintains that the intermediate to felsic intrusive sequence at these magmatic-hydrothermal centers is the product of a single fractionating magma chamber at depth. It is based on chemical and isotopic trends of intrusions at various deposits, for example Sierrita (Anthony and Titley, 1988). Such a model is strengthened by studies, such as at Yerington, combining robust radiometric ages with unusual exposures of mineralizing porphyries and the parent magma chamber (Dilles, 1987; Dilles and Wright, 1988). At Yerington, the ages of the batholith and derivative porphyries are consistent with the time of crystallization of magma chambers as constrained by thermal models. In this single-event model, porphyry copper mineralization is related to a single, short-lived magmatic/thermal event.

In many porphyry systems in southwestern North America, K-Ar ages of the igneous rocks span periods longer than probable thermal lifetimes of single magma chambers. This likely suggests that the intrusions were derived from separate magma chambers that had crystallized completely before a younger one formed. If mineralization resulted from hydrothermal systems related to multiple magma batches, then many of the porphyry copper deposits formed from multiple, superimposed events. The multiple event model has been suggested by studies at Butte (Meyer et al., 1968), Chuquicamata (Ballard et al., 2001; Reynolds et al., 1998), the Indio Muerto district (Gustafson et al., 2001), and the Potrerillos district (Marsh et al., 1997).
Sub-solidus closure temperatures for the K-Ar system make it susceptible to partial or complete resetting in a repeatedly thermally-active porphyry copper intrusive center, thus K-Ar (and Ar-Ar) dates can represent later events, not the magmatic or high-T hydrothermal events. Moreover in rocks of Laramide age, error estimates of analyses of separate intrusions are large enough to make the ages analytically indistinguishable from one another. The temporal evolution of these systems individually and regionally could be better evaluated with ages from the more robust U-Pb zircon isotopic system.

The purpose of this study is to evaluate the timing of magmatism and mineralization in the Pima mining district, Arizona by acquiring accurate and precise U-Pb crystallization ages of intrusions associated with the Sierrita deposit. In doing so, I intend to determine, first, the duration of magmatism at Sierrita and if the mineralization is the product of a single or multiple events, and, second, if the age of mineralization-related magmatism falls into one of the discrete time intervals identified for the southwest North America porphyry copper province. If mineralization turns out to be restricted in time throughout the province, then the implication is, as McCandless and Ruiz (1993) suggested, that there may be a tectonic control on the ascent of productive magmas into the upper crust or accumulation of metals in the lower crust. If the intrusions are the product of a single magma chamber, then the implication is that the parent magma chamber is large, and size may be a fundamental control on the formation of a porphyry copper deposit.

The Sierrita deposit is an exceptional deposit for this study for the following reasons. Sierrita has good exposure and with many published studies (and many more theses) at
the deposit and district scale (Cooper, 1960; Cooper, 1971; Cooper, 1973; Preece and Beane, 1982; Titley, 1982b; Titley et al., 1986; West and Aiken, 1982). Sierrita has a diverse suite of intrusive rocks, which cover the spectrum of a typical intermediate to felsic magmatic arc sequence (Lang and Titley, 1998). Extensive geochemical (major, trace, and isotopic element) analyses have been conducted on these rocks (Anthony and Titley, 1988). Additionally, rocks in the deposit and district have been dated with the K-Ar and Re-Os isotopic systems, confirming the relative ages of intrusion, and providing information about the thermal and mineralization history (Creasey and Kistler, 1962; Damon et al., 1964; Cooper, 1973; Marvin et al., 1973; Shafiqullah and Langlois, 1978; McCandless and Ruiz, 1993; Jensen, 1998). The mineralizing intrusion at Sierrita is thought to be known and is exposed. Furthermore, the minimal affects of pervasive acid and supergene alteration mean that hypogene alteration is well-documented (West and Aiken, 1982) and that nearly fresh samples can be obtained for analysis.

Regional Geology

The southwestern North American porphyry copper province is located in the Basin and Range and Central Mountain physiographic regions of Arizona, Sonora, and New Mexico, and extends approximately 750 km northwest-southeast by 400 km southwest-northeast (Figure 1). The province occurs on the southwestern margin of the North American craton and formed during the Laramide orogeny from about 80 – 50 Ma (Titley, 1993). At this time a magmatic arc evolved above the inferred continental margin as a result of subduction of the Pacific plate beneath the North American plate (Coney, 1978). Subduction-related, calc-alkaline magmas, with which the porphyry
Figure 1. Map of Arizona-New Mexico-Sonora porphyry copper province showing the location of deposits. Square shows the location of the Pima district (figure 2). Numbers are Re-Os mineralization ages from McCandless and Ruiz (1993). Figure after Titley (1993).
copper deposits are associated, intruded a column of Proterozoic basement of mixed volcanic, clastic, and granite rocks, overlain by Paleozoic carbonate rocks and Mesozoic clastic, volcanic, and intrusive rocks (Titley, 1993). The basement has been divided into different provinces on the basis of age, lithology, geochemistry, geophysics, and isotopes, such as Pb and Nd (Bennett and DePaolo, 1987; Wooden et al., 1988; Chamberlain and Bowring, 1990; Wooden and Tosdal, 1990; Lang and Titley, 1998; Bouse et al., 1999; Eisele and Isachsen, in press). Figure 1 shows the locations of the province and individual porphyry copper deposits, including Sierrita-Esperanza.

The complicated superposition of Miocene core-complex and Basin and Range extensional deformation has made the structural setting of the porphyry province during the Laramide difficult to define. Nevertheless, Davis (1979) has described west to northwest-striking reverse and thrust faults, as well as regional folds with sub-horizontal west-northwest to north-northwest trending fold axes for the Laramide of southeastern Arizona. He has explained them with a basement-cored uplift model that requires a southwest to northeast-oriented regional compressive stress. Rehrig and Heidrick (1972) and Heidrick and Titley (1982) documented the orientations of joints, veins, faults, and dikes in and around Laramide intrusions related to productive and non-productive porphyry systems. They found systematic orientations of east-northeast and north-northwest strikes at all intrusions studied and attributed them to an east-northeast-directed regional compressive stress. Both studies demonstrate a stress that is consistent with the plate tectonic history of the Laramide (Coney, 1976). The effect of pre-Laramide structures on the evolution of the Laramide deformation and intrusion is mainly one of
speculation and is reviewed by Titley (1982a). A northeast structural grain in the
Precambrian basement of Arizona is thought to exert a control on the location and
elongation of intrusions. Furthermore, a northwest trend in the evaporites of the
Paleozoic section parallels the regional structural trend of the Laramide. Cause and
effect, however, has not been confidently demonstrated between pre-Laramide and
Laramide deformation.

Laramide intrusive complexes throughout the province exhibit similar trends in
composition, texture, and relative timing of mineralization. A typical igneous sequence
consists of early andesitic and dacitic, volcanic rocks followed by later intrusions that
progress from diorite through quartz monzonite and granodiorite to granite. The
intrusions follow a textural trend from equigranular to porphyritic. Mineralization is
coincident with felsic, porphyry intrusions that form near the end of the igneous cycle
(Titley and Beane, 1981; Titley, 1993). These similarities occur regardless of the
duration or absolute age of inception and termination of magmatism at an intrusive center
(McCandless and Ruiz, 1993; Lang and Titley, 1998).

**Regional Geochronology**

Laramide magmatism, alteration, and mineralization have been extensively dated
since the early 1960’s but primarily by K-Ar studies (Creasey and Kistler, 1962; Damon
et al., 1964; Damon and Mauger, 1966; summarized in Reynolds et al., 1985).
Exceptional studies at the district-scale include those of Creasey (1980) for the Globe-
Miami district and Shafiqullah and Langlois (1978) for the Pima district. Since 1990,
there have been a handful of Re-Os studies conducted in the province (McCandless and
Ruiz, 1993; Jensen, 1998). The early geochronology established the Laramide age of the Arizona-New Mexico-Sonora copper province and, importantly, supported the genetic link between intrusive activity and porphyry copper mineralization and alteration. The dates also show that the absolute ages of initiation and termination of magmatism vary from intrusive center to center. Centers were active—at least sporadically—anywhere from 1 to 20 m.y., and the time elapsed between the onset of magmatism and mineralization varies as well.

Despite these differences, other trends in the ages have been used to evaluate regional metallogenesis. A simple trend in mineralization-related plutons is a general decrease in age from northwest to southeast (Livingston, 1973). Livingston et al. (1968) reported the ages of 15 mineralizing porphyries in a histogram, which showed that the majority of the ages clustered around 60-55 Ma. In a figure from Damon and Mauger (1966), the ages of 7 out of 13 Laramide plutons from porphyry deposits (no distinction between mineralizers or hosts) fell between 65-60 Ma. These early studies suggest that certain times during the evolution of the arc may have been more favorable for porphyry copper mineralization.

This conclusion was supported and elaborated upon by the study of McCandless and Ruiz (1993). They dated molybdenite from several porphyry copper deposits using the Re-Os isotopic system to constrain the timing of mineralization. Assuming that molybdenum and copper mineralization are essentially coeval, they found that sulfide mineralization occurs in the final stages of magmatic activity at a deposit and that different deposits have nearly identical ages for mineralization. They identified two
discrete intervals from 74-70 Ma and 60-55 Ma into which the ages of mineralization fell but suggested that there was possible evidence for an interval at approximately 64 Ma. By observing that deposits with similar mineralization ages differed in age of onset, duration, and magnitude of associated magmatism, they concluded that mineralization, presumed previously to be controlled by local processes, was in fact triggered by regional-scale events. They went on to suggest that the crust may be acting as a filter, where a minimum amount of time is required for metals to accumulate to economic levels in magmas and that a tectonic event may trigger their ascent into the upper crust. Their Re-Os ages are included in Figure 1.

**Geology of the Pima District, Sierrita Mountains**

The Pima district is located about 20 miles south-southwest of Tucson, Arizona, in the eastern half of the Sierrita Mountains and includes outcrops in the alluvium east of the mountains to the Santa Cruz River (Figure 2). The district is the site of four open pit mines of porphyry copper and copper skarn mineralization related to Laramide plutons: Sierrita-Esperanza, Twin Buttes, Pima-Mission, and San Xavier North. The district produces copper, molybdenum, silver, and minor zinc. Deposit types include disseminated porphyry, skarn, massive carbonate replacement, and vein-controlled base and precious metals in clastic, carbonate, volcanic, and silicate intrusive rocks (Titley, 1982b). The mountains consist mostly of Mesozoic volcanic and clastic rocks and Laramide intermediate to felsic intrusions, with smaller bodies of Precambrian and Mesozoic granitoids and Tertiary volcanic rocks. The outcrops just east of the mountains contain
Figure 2. Simplified geology of the Pima District showing the Sierrita-Esperanza (SE), Twin Buttes (TB), and Pima-Mission (PM) orebodies. Also shown are representative strikes and dips for some volcanic and sedimentary units, and the spatial distribution of K-Ar ages in the Ruby Star granodiorite batholith. Ages at Twin Buttes and Pima-Mission are for quartz monzonite porphyry and a sericite vein in quartz monzonite porphyry, respectively. The square outlines the approximate location of figure 3. After Cooper (1973).
the Paleozoic carbonate section, as well as Pre-Cambrian and Laramide plutons and Mesozoic and Tertiary clastic and volcanic rocks. Evidence exists for multiple episodes of deformation, but most of the pre-Laramide and Laramide deformation is obscured by mid-Tertiary tectonism (Titley, 1982b).

**Lithology and Stratigraphy**

Laramide plutons intrude Precambrian crystalline rocks, Paleozoic carbonate and clastic rocks and pre-Laramide Mesozoic intrusive, volcanic and clastic rocks. Mid-Tertiary volcanic and clastic sedimentary rocks unconformably overlie them. The Precambrian rocks are granodiorite and quartz monzonite with minor diorite and granite (Cooper, 1973). The unconformably overlying Cambrian through Permian section contains a basal clastic portion but consists of mainly carbonate sedimentary rocks with gypsum-dominated evaporites near the top. This section hosts mineralization in the Pima-Mission and Twin Buttes deposits and is the same as the Paleozoic section found throughout southern Arizona (Titley, 1982b).

The majority of the Sierrita Mountains consists of Mesozoic and Tertiary igneous rocks. The oldest rocks of the Mesozoic section are the Ox Frame Volcanics of Triassic age. They consist of andesitic to rhyolitic lava flows, breccias, and pyroclastic rocks and are found in kilometers-scale outcrops towards the southern end of the district. They are an important host to mineralization in the southern part of the Sierrita-Esperanza mine. A Triassic sedimentary unit called the Rodolfo Formation unconformably overlies the Paleozoic section in the Pima-Mission mine portion of the district and contains clasts of the Ox Frame Volcanics.
The Ox Frame Volcanic rocks are intruded by the Harris Ranch quartz monzonite, an Early Jurassic (190 Ma), fairly extensive, felsic granitic unit. It, too, hosts mineralization in the western part of the Sierrita-Esperanza mine. Another Jurassic pluton, the Sierrita granite (150 Ma), is present mainly north of the Harris Ranch quartz monzonite.

Cretaceous conglomerates, quartzites, and arkoses of the Angelica Arkose are exposed in fault contact with the Paleozoic and Mesozoic sections near the Twin Buttes and Pima-Mission mines.

*Laramide igneous rocks*

Laramide (68-60 Ma) igneous rocks consist of sparse andesitic to rhyolitic volcanic rocks, hypabyssal intrusions, and voluminous equigranular to porphyritic granodiorites to granites. Oldest of the volcanic package are the Demetrie Volcanics (67 Ma, C. Fridrich, pers. comm., 2001), which are primarily andesite and dacite lava flows, lahars, and tuffs, with minor rhyolitic phases. These rocks are found in the southern and western parts of the Sierrita Mountains, where they more commonly overlie the older Mesozoic volcanic rocks and dip approximately 60° to the south (Fig. 2). In the west, the Demetrie Volcanics are overlain by the Red Boy Rhyolite, the youngest exposed Cretaceous unit. The Red Boy Rhyolite is a section of rhyolitic to dacitic lavas and pyroclastic rocks.

The oldest of the Laramide age rocks are the northwest trending bodies and smaller scattered pods of biotite quartz diorite that intrude the Harris Ranch quartz monzonite in the Sierrita-Esperanza mine. The largest Laramide unit exposed in the district is the Ruby Star granodiorite, a composite batholith with equigranular and porphyritic phases. It has a north-northwesterly trend and is exposed from north to south for about 20 km.
Porphyries associated with mineralization at the Sierrita-Esperanza deposit occur at the southern end of the Ruby Star granodiorite and intrude the quartz diorite and Ox Frame Volcanics. These porphyries include quartz monzonite, granodiorite, rhyodacite, quartz latite, and granite porphyries and are variably mineralized. Almost due east of Sierrita-Esperanza is another group of porphyritic dikes, which intrude the Paleozoic and Mesozoic section at the Twin Buttes deposit. A similar porphyry suite intrudes the Paleozoic and Mesozoic sections at the Pima-Mission and San Xavier North deposits. The similarities of these deposits to the Twin Buttes deposit led Cooper (1960) to interpret them as faulted slices of a single porphyry system.

Mid-Tertiary rocks are the youngest rocks exposed in the district. A thick sequence of Oligocene clastic and volcanic rocks known as the Helmet Fanglomerate lies between the Twin Buttes and Pima-Mission deposits. The fanglomerate, dated at approximately 30 Ma (Damon and Bikerman, 1964), consists of a 3000m-thick section of landslide blocks, conglomerate, and arkosic sandstones with interlayered volcanic lava flows, tuffs, and breccias. Beds dip between 20 and 64° to the south to southeast and generally steepen northward, i.e., deeper in the stratigraphic sequence and away from the main bounding fault.

A series of Miocene-age mainly volcanic and volcaniclastic rocks called the Tinaja Peak Formation are deposited above the Demetrie Volcanics south of the Sierrita-Esperanza mine. The volcanic rocks range from rhyodacite to andesite lavas, tuffs, and breccias; the volcaniclastic rocks are conglomerates. This unit dips 10-30° mainly to the south and southeast (Cooper, 1973; Lipman and Fridrich, 1990).
Structure

The structure of the Pima district is the result of complexly superimposed
deformation events, the youngest of which obscures the oldest and is best preserved.
Late Paleozoic or Early Mesozoic deformation is expressed by a depositional contact of
Mesozoic rocks over the recumbently folded and overturned Paleozoic section at Twin
Buttes and Pima-Mission mines. Mesozoic rocks are folded with a northwest-striking
axis at these deposits, as well as at San Xavier North. These folds are thought to have
formed during the Late Cretaceous and are consistent with a northeast-southwest oriented
compressive stress (Barter and Kelly, 1982; Jansen, 1982). Laramide faults include
north-northwest trending thrust faults and east-northeast trending faults with both dip-
and strike-slip motion (Lipman and Fridrich, 1990). Veins in the Sierrita deposit are
preferentially aligned along these trends, which are also consistent with northeast-
southwest oriented compressive stresses (Heidrick and Titley, 1982).

The most prominent structural feature of the district is the mid-Tertiary, north and
east striking, low-angle San Xavier fault. Based on similarities in lithology, outcrop
geometry, and structural features between the Pima-Mission deposit in the hanging wall
and the Twin Buttes deposit in the footwall, Cooper (1960) concluded that Pima-Mission
was the upper portion of Twin Buttes and had been transported northward about 10 km
along this fault. Cooper interpreted it as a thrust fault. Lacy and Titley (1962), in turn,
considered it a gravity slide fault with eastward transport of the hanging wall. Seedorff
(1983) and Lipman and Fridrich (1990) interpreted it as an originally high-angle normal
fault rotated to its present low angle during southward tilting of the district. Finally,
Jensen (1998) called it a low-angle detachment fault with little or no rotation, cut by later normal faults.

Tilting/Rotation of the District

The nature of the San Xavier fault is part of the larger question of Cenozoic district-scale tilting, namely if any has occurred and in what amount and direction. In one camp, the Pima District is considered upright. In another, it is considered to have been tilted 30-60° to the south-southeast about an east-northeast axis of rotation. Many observations can be explained in ways that support or do not discredit either hypothesis.

Arguments for tilting begin with structural and stratigraphic observations. The Miocene Tinaja Peak Formation, exposed at the southern end of the Sierrita Mountains, dips 10-30° to the south. The Oligocene Helmet Peak Fanglomerate strikes east-northeast and dips between 20 and 64° to the south. Cretaceous volcanic rocks, including the Red Boy Rhyolite and the Demetrie Andesite, dip 40-60° to the south to south-southeast. Their strikes are consistent with the trend of the unconformity between these rocks and the underlying Triassic Ox Frame Volcanics. Pegmatites, thought to be sills, intruding the northern end of the Ruby Star granodiorite batholith dip 20° to the south. The beds and sills are presumed to be originally horizontal features; their present southward dips are evidence for regional southward tilting. Furthermore, Precambrian rocks always crop out north of stratigraphically younger units. Triassic volcanic and sedimentary rocks and a Jurassic granite are increasingly metamorphosed to the north (Seedorff, 1983; Lipman and Fridrich, 1990). Finally, a study of hornblende barometry in the Ruby Star Granodiorite showed that the northwestern end crystallized at 13 km and
southern and eastern ends at 7 km (Jensen, 1998). These last three observations suggest that north represents deeper stratigraphic and structural levels, which were exposed by southward tilting and erosion.

An interpretation of southward tilting from observations about the porphyry system is based on the model that these systems are intruded vertically and have certain characteristics from bottom to top (Sillitoe, 1973). To begin with, the porphyry intrusions are located at the southern end of the Ruby Star granodiorite batholith, along trend with its porphyritic phase, which grades into the main porphyry body at Sierrita. A zone of high pyrite and more intense sericitic alteration is located at the southern end of the porphyry complex and partly in the volcanic host rocks just south. A weakly mineralized stock of granite porphyry appears to plunge toward the north into the main porphyry body (this study). Higher-grade mineralization is present in the main porphyry body beneath the presently north-dipping contact of the two porphyries (Seedorff, 1983; this study). These observations suggest, that south is up in the system and that the system was tilted toward the south and eroded to attain its present geometry.

The observation that the San Xavier fault is presently flat lying and that it has accommodated approximately 10 km of normal displacement suggest, by analogy, that it was tilted and originally steeper (cf. Proffett, 1977). Seedorff (1983) compares this fault to others with similar displacement in the western U.S. that have been shown to undergo simultaneous tilting. He also compares the San Xavier fault to other normal faults that were shown to originate as high-angle faults, and says that southward tilting would explain the fault’s present orientation if it had an initial steep dip.
Jensen (1998) most recently studied the district and concluded that it was untilted. A structural study of faults in the mine area indicated stress directions that were nearly horizontal and vertical, which Jensen considered evidence that the deposit was upright. He stated that based on his observations the Miocene rocks did not dip uniformly to the south, but rather to the south and west and, in some cases, not at all. He explained dips in the Helmet Fanglomerate by rotation of only the hanging wall of the San Xavier Fault rather than tilting of the entire district. Laramide compressive stress or “shouldering effects” of the intrusion of the Ruby Star Granodiorite accounted for southward dips of the Cretaceous volcanic rocks. He explained the apparent shallowing structural levels toward the south indicated by metamorphism and hornblende barometry as a result of unmapped north-south striking, east dipping normal faults cutting bodies with a northwest trend. As far as the porphyry system is concerned, he reported that porphyry plugs and dikes are vertical in the pit, and used small-scale block rotations in the Esperanza pit, based on his structural study, to account for the different alteration mineralogy and overall position in the system there.

**Geology of the Sierrita-Esperanza area**

The Sierrita-Esperanza deposit is centered on a suite of Laramide porphyritic intrusive rocks hosted by Mesozoic volcanic rocks and granitoids (Fig. 3). These rocks and other aspects of the deposit are extensively described in several articles (Preece and Beane, 1982; West and Aiken, 1982; Titley et al., 1986; Jensen, 1998) and form the basis of the following description. Mesozoic host rocks consist of the Triassic Ox Frame Andesite and Rhyolite Formations and the Jurassic Harris Ranch quartz monzonite.
Figure 3. Simplified geologic map of the Sierrita-Esperanza deposit showing the Sierrita (S), Esperanza (E), and Ocotillo (O) pits. Abbreviations for geochronology samples: Rsgd = Ruby Star granodiorite, Qmp = quartz monzonite porphyry, Gp = granite porphyry, Qlp = quartz latite porphyry dike. (Phelps Dodge Sierrita geology department, 1998)
Laramide intrusive rocks form a sequence that becomes progressively more felsic with time. The first intrusive event is the biotite quartz diorite. The diorite was intruded by the Ruby Star granodiorite, the batholithic body in the district. The batholith grades southward into the quartz monzonite porphyry, the main porphyry body, which occurs in and around the pit. An igneous breccia intrudes the quartz monzonite porphyry, as does the Sierrita granite porphyry stock. It is not clear whether the breccia is the intrusive contact between two porphyries or a separate intrusive unit. The Sierrita granite porphyry is intruded by a smaller plug of rhyodacite porphyry. All Laramide intrusive rocks are cut by a series of quartz latite porphyry dikes.

**Laramide Igneous Rocks**

The biotite quartz diorite occurs at small plugs that crop out along a northwest trend. The largest body is found at the western end of the pit, but smaller bodies are found in and around the pit as well. It is black to dark green, fine grained, and equigranular, and contains mainly plagioclase feldspar, pyroxene, and hornblende, with lesser quartz. Secondary biotite replaces hornblende, and K-feldspar is seen as rims on the plagioclase. This unit was a chemically favorable host for mineralization and contains some of the best grades in the deposit, particularly at the contact with the quartz monzonite porphyry.

The Ruby Star granodiorite occurs north of the Sierrita-Esperanza pits and is a composite intrusion with a central porphyritic facies that grades into an equigranular border facies (Lovering et al., 1970). The equigranular phase is a light to medium gray, medium-grained rock containing mainly plagioclase, K-feldspar, and quartz with biotite and lesser hornblende, sphene, zircon, apatite, and magnetite. The porphyritic phase is
distinguished by pink K-feldspar megacrysts, 1-3 cm long, set in a light gray groundmass. The Ruby Star granodiorite hosts mineralization at the eastern contact of the Quartz Monzonite porphyry in the Ocotillo pit.

Just north of the Sierrita pit, the porphyritic phase of the Ruby Star granodiorite grades into the quartz monzonite porphyry. In the Ocotillo pit (Figure 3), the quartz monzonite porphyry has a sharp contact with the equigranular phase of the Ruby Star. The porphyry contains orthoclase, biotite, and quartz-eye phenocrysts in an aphanitic groundmass of plagioclase, K-feldspar, and quartz. The textural variety of this unit in the eastern part of the mine is distinguished by large (2-3 cm) orthoclase phenocrysts and abundant, coarse-grained biotite books. Towards the west, the texture is characterized by smaller orthoclase phenocrysts and less abundant biotite. West and Aiken (1982) reported that this porphyry is considered the main mineralizer.

The Sierrita granite porphyry intrudes the quartz monzonite porphyry west of the Sierrita pit and north of the Esperanza pit (Fig. 3). It is distinguished from the quartz monzonite porphyry by more abundant quartz eyes, smaller orthoclase phenocrysts, and smaller, less abundant biotite phenocrysts in an aphanitic groundmass of quartz, orthoclase, and plagioclase. It is called the “barren” or low-grade core of the system and is only weakly mineralized.

The breccia also cuts the quartz monzonite porphyry. It lies mainly to the west of the granite porphyry in the center of the Sierrita pit, but it is also exposed north and south of the granite porphyry in thin, adjacent, rind-like bodies. The matrix is igneous but texturally distinct from the quartz monzonite and granite porphyry, in that it lacks both
orthoclase phenocrysts and conspicuous quartz eyes but contains mainly fine-grained biotite, quartz, rock flour and minor local magnetite. Clast type depends on the adjacent rock unit, and clast abundance ranges from 5-10% in the core to 50-60% in the rim. The breccia contains some of the best mineralization in the mine.

The rhyodacite porphyry was intruded into the granite porphyry stock just northeast of the main body. It is characterized by 5-10 mm plagioclase phenocrysts, 0.5-1.5 mm biotite phenocrysts, and subhedral to anhedral quartz in a groundmass too small to be identified. The rhyodacite is weakly mineralized.

The quartz latite porphyry dikes range in width from one to twelve feet and contain small sub-centimeter plagioclase and orthoclase phenocrysts in a light to dark gray quartz-feldspar groundmass. Biotite phenocrysts are occasionally present.

**Hydrothermal Alteration**

There are at least three distinct centers of hydrothermal alteration and mineralization in the Pima district — the Red Boy rhyolite center, the Sierrita-Esperanza porphyry center, and the structurally dismembered Twin Buttes-Pima-Mission-San Xavier North center (Titley, 1982b; Titley et al., 1986). Styles of hydrothermal alteration and copper mineralization reflect the host rocks, but can be broadly grouped into several types of alteration. Potassium silicate alteration, characterized by quartz-orthoclase-biotite veinlets and vein envelopes is developed in each area. Skarns dominate the carbonate-hosted mineralization in the Twin Buttes - Mission-Pima center (Barter and Kelly, 1982; Jansen, 1982).
At Sierrita, an early potassic stage of alteration is primarily represented by quartz-orthoclase-chalcopyrite-pyrite-molybdenite vein selvage assemblages and by biotitization of groundmass and mafic minerals in intermediate hosts. Also associated with this early phase of alteration is a separate alteration of vein or selvage albite. It is followed by less abundant quartz sulfide veining with quartz sericite envelopes. Propylitic alteration takes the form of mainly epidote veins with granular pyrite, calcite, quartz and chlorite. Late quartz-sphalerite-galena, molybdenite, and gypsum veins cut previous vein types (West and Aiken, 1982). Within a few kilometers north of the mine, as the abundance of K-silicate and other sulfide-bearing veins drops off, sodic plagioclase stable alteration (with variable epidote, chlorite, actinolite, pyrite ± quartz) is prominent in the eastern part of the Ruby Start granodiorite, particularly near the contact with the country rocks (Cooper, 1973).

West of the Sierrita mine in the Red Boy center, Titley et al. (1986) observe two sets of veins in the Jurassic, Triassic, and Cretaceous rocks, predating the main Laramide hydrothermal system of the Sierrita-Esperanza porphyries. They consist of epidote-quartz±tourmaline fillings with orthoclase-epidote selvages and quartz-epidote-sulfide veins.

**Grade distribution and implications for timing of mineralization**

In order to better understand the relative timing of hydrothermal activity and magmatism within the Sierrita center, selected diamond drill holes were examined for cross cutting relationships in conjunction with an analysis of grade and lithologic information from Sierrita’s drill hole database.
The broad patterns from the mine database provide evidence for a systematic relationship between rock types, contacts and grades (cf. West and Aiken, 1982). Figure 4 shows the relationship between lithology and hypogene copper grade. The highest grades of hypogene mineralization are consistently in the diorite and Oxframe andesite. This reflects a favorable chemistry of the host for copper deposition. The quartz monzonite porphyry and the breccia have consistently higher copper grades (0.2-0.4 %) than the granite porphyry (<0.1%). The drop in grade across the contacts from the quartz monzonite porphyry and breccia to the granite porphyry is for the most part abrupt. This relationship suggests that mineralization is associated with the quartz monzonite porphyry and mainly predates intrusion of the granite porphyry although a minor amount is contributed by it. The late rhyodacite porphyry contains yet lower grades and vein abundances and the youngest intrusive rocks, the quartz latite porphyries are barren with only sparse pyrite veinlets and alteration.

In order to confirm this relationship, mineralized veins present in the quartz monzonite porphyry would have to be observed being truncated by the granite porphyry. Such relationships have not been observed. Other possibilities are that mineralization is associated approximately equally with both porphyries or mainly with the granite porphyry. In these cases, respectively, the grade distribution would show the highest grade near the contact of the two porphyries or increase gradually from the granite porphyry into the quartz monzonite porphyry.
Figure 4. N-S section through Sierrita pit along E96500 showing lithology and distribution of hypogene copper grade.
**Previous Geochronology in the Pima District**

The geochronology of the Laramide intrusive and hydrothermal events at Sierrita has been approached using the K-Ar and Re-Os isotopic systems. Published dates suggest that intrusive activity, hydrothermal alteration, and mineralization spanned 16 m.y. (Figure 5). Generally speaking, although the dates are consistent with the sequence of crosscutting relationships and indicate that magmatism and hydrothermal activity are broadly coeval, they do not unambiguously define the temporal evolution of the system.

Multiple dates on the same geologic unit commonly diverge, for example, three dates on the Ruby Star granodiorite are 63.1, 61.6, and 60.1 Ma. Biotite and feldspar from the same hydrothermally altered diorite yielded ages of 61.6 and 57.5 Ma respectively. K-Ar results have relatively large errors and are subject to thermal resetting, thus they do not resolve closely spaced events and require interpretation in the context of the overall thermal history. The typical error estimate of 2 m.y. for a K-Ar date does not allow possibly separate events to be resolved nor the true temporal separation to be known when events are in fact separate. For example, at ± 2.0 Ma, it is uncertain if the quartz monzonite porphyry (58.4 Ma) and quartz latite porphyry dikes (58.0) are close in time or separated by 4 m.y. This is relevant when considering a genetic relationship between intrusive units.

Re-Os ages on molybdenite (Fig. 5) span 7 m.y., with the first published date (McCandless and Ruiz, 1993) at 56.2 ± 1.8 Ma and the more recent work by Jensen (1998) giving 63.5 ± 0.3 for veins in quartz monzonite porphyry and three dates of 60.0-
Figure 5. Summary of previous K-Ar, U-Pb, and Re-Os geochronology of Laramide intrusion, alteration, and mineralization at Sierrita-Esperanza, including ages of Ruby Star Granodiorite north of mine in lower plate of San Xavier fault.

60.8±0.3 Ma on samples from the granite porphyry. The latter dates are consistent with the U-Pb work presented below, whereas there are inconsistencies in some of the K-Ar or earlier Re-Os ages of magmatism and hydrothermal activity. For example, a crystallization age of 58.4±2.0 Ma based on K-Ar of igneous biotite in the QMP is neither consistent molybdenite mineralization date in the same unit of 63.5±0.3 Ma. nor with a date on hydrothermal biotite of 64.0±2.0 Ma. These inconsistencies could call the quality of the ages into question. On the other hand, these absolute ages could point to a greater complexity of magmatic and hydrothermal events than has been documented with field relationships.

**U-Pb studies**

In order to help resolve the thermal history of the system, U-Pb dating of selected igneous rocks was undertaken. The results reveal that there were multiple events, and many of the discrepancies in the published dates can be rationalized by spatially controlled zones of resetting related to younger events.

**Methods**

20 kg samples were taken from intrusions within the pit. Sampling location was based on ready accessibility to bench faces where care was taken to sample in-place material rather than bench-face talus. No sample was entirely fresh, as all contained disseminated pyrite, chalcopyrite, and molybdenite mineralization, but an effort was made where possible to avoid samples with obvious veins of K-feldspar and quartz alteration. Sample locations are indicated with stars in figure 3.
U-Pb analytical methods, from physical separation of zircons to calculation of isotopic ages, were done at the University of Arizona following the methods reported in Eisele and Isachsen (in press).

**New U-Pb Ages**

Multiple fractions of zircon separates from four intrusive phases were dated by conventional U-Pb methods (Table 1, Figure 6). Ages based on concordant analyses are interpreted as crystallization ages. Most samples contained discordant as well as concordant fractions; the discordant fractions likely reflect inheritance given that their ages define chords with upper intercepts consistent with the regional basement.

The most extensive Laramide unit in the district, the Ruby Star Granodiorite yielded two concordant and two nearly concordant fractions. The fractions are single- to two-grain analyses of translucent, inclusion-poor, colorless, euhedral, short, bipyramidal zircons. The average 206Pb*/238U age is 64.3 ± 0.4 and is interpreted as the crystallization age.

The age of the quartz monzonite porphyry was based on the analyses of short, euhedral, colorless, inclusion-free, translucent zircons. Three fractions yielded two concordant points and one slightly discordant point with an inherited component. The weighted mean of the two concordant points is 63.3 ± 0.2. A York fit of the three points gives a lower intercept of 63.4 ± 0.3 and an upper intercept of 1440 ± 260. Because the upper intercept is consistent with the basement geology of this region (the presumed source for the inherited component) and the lower intercept gives the same age as the concordant points, 63.4 ± 0.3 is taken as the crystallization age.
The Sierrita granite porphyry contained clear, colorless, inclusion-poor, short, euhedral zircons. Two concordant analyses give a $^{206}\text{Pb}*/^{238}\text{U}$ age of $60.5 \pm 0.2$. The discordant point is not used to define a chord since its isotopic ratios seem to be the product of complex lead loss. The age of the concordant analyses is interpreted to be the crystallization age.

The quartz latite porphyry dikes had very similar zircons, with the exception that some of those analyzed were proportionately longer. The age for this unit comes from one nearly concordant analysis and an interpretation of four reversely discordant analyses. The reverse discordance of the analyses resulted from low measured $^{206}\text{Pb}/^{204}$ ratios and can be explained by contamination from lab chemical organics or high common Pb in the zircons. Ages were extrapolated by artificially increasing the error of the measured $^{206}\text{Pb}/^{204}$ ratios until the error ellipses of an analysis intersected the concordia curve. The $^{206}\text{Pb}*/^{238}\text{U}$ ages of the point of intersection of the ellipses with concordia was taken to be the best-estimate age of the sample. The consistency of the extrapolated ages (59.2, 60.1, 60.8, and 60.9) suggests that these ages are probably real. The weighted mean of all fractions is $60.7 \pm 1.3$ Ma. Given the relative age relations indicating that this unit is younger than the Sierrita granite porphyry, the maximum age of this unit is lowered to 60.7 Ma (the maximum age of Sierrita granite porphyry).

In summary, the age of the Ruby Star granodiorite batholith is $64.3 \pm 0.4$ Ma, followed closely by the quartz monzonite porphyry at $63.4 \pm 0.3$ Ma. The next porphyry
Figure 6. Concordia diagrams showing U-Pb (zircon) data for the Ruby Star Granodiorite (Rsg), the Esperanza quartz monzonite porphyry (Eqm), the Sierrita granite porphyry (Sgp), and the quartz latite porphyry dikes (Qlp). The ages are 64.3 ± 0.4, 63.5 ± 0.3, 60.5 ± 0.2, and 60.7 ± 1.3 Ma, respectively.
unit, not including the breccia, crystallized at 60.5 ± 0.2 Ma shortly before magmatism terminated with the intrusion of the quartz latite porphyry at ~60 Ma. Duration of Laramide magmatism at the Sierrita intrusive center therefore is about 8 m.y. (based also on the K-Ar age of the quartz diorite). Two periods of apparent quiescence, each lasting 2-3 m.y., occurred during the development of the deposit.

**Discussion**

*Geochronology in the Pima District*

The new U-Pb crystallization ages are consistent with the relative intrusive sequence given by K-Ar ages and crosscutting relationships observed in the field. They are more accurate, precise, and better explain some of the alteration and mineralization ages than the K-Ar crystallization ages.

A comparison of the U-Pb ages with the K-Ar crystallization ages (Figure 7) shows that the former are generally older than the latter or, in the case of overlap, fall at the older end of the K-Ar error estimates. Most notable in this respect is the quartz monzonite porphyry, whose U-Pb age turns out to be 3-5 m.y. older than previously known. This pattern is consistent with the notion that a zircon age represents a more accurate crystallization age by virtue of its ~750° closure temperature with respect to U and Pb.

The local and district-scale patterns in K-Ar ages can be reinterpreted in light of these results and an assumption, based on the evidence cited above, for mid-Tertiary tilting. The younger average K-Ar ages can be explained by the ~300° and ~250° closure
Figure 7. Geochronology comparison diagram for this study's U-Pb ages, previous K-Ar ages of same units, and Re-Os mineralization ages. Re-Os ages are for molybdenite veins in stock with which they are grouped or in immediately adjacent host rock. See table 1 for U-Pb analytical data, and figure 5 for abbreviations, references, and more details about K-Ar and Re-Os ages.
temperature of biotite and feldspar, respectively. The K-Ar ages thus represent the time at which these minerals cooled below this temperature. Therefore, the northward younging K-Ar ages of the Ruby Star granodiorite (Figure 2) may correspond to longer cooling associated with greater paleodepth. This supports the hypothesis that the district is in fact tilted to the south and is inconsistent with the hypothetical down to the east normal faults proposed by Jensen (1998). Another explanation for the younger K-Ar ages could be complete or partial resetting by later thermal activity that heated the biotite and feldspar above their closure temperatures. These scenarios most likely combine to explain the K-Ar ages at the intrusive center because it was thermally active during the Laramide and mid-Tertiary.

The U-Pb ages are also more precise than the K-Ar ages, as seen by error estimates between 0.3 - 0.7 m.y. compared to 2 m.y. Overlap in ages across units is thus reduced, and units whose previous ages were analytically indistinguishable can now be resolved with greater certainty. For example, the Ruby Star granodiorite, the quartz monzonite porphyry, and quartz latite porphyry dikes, whose ages overlapped by 2 m.y., now have ages that do not overlap. This precision highlights the rocks' separation in time and allows for a meaningful evaluation of genetic relationships.

Finally, the new crystallization ages appear to resolve some of the age inconsistencies between mineralization/alteration and magmatism (Figure 7). Specifically, the new age of the quartz monzonite porphyry (63.4 ± 0.3) coincides with the oldest molybdenite age of mineralization (63.5 ± 0.3). The 62-64 Ma biotite alteration ages can also be accounted for by the new quartz monzonite porphyry age. The age of the granite
porphyry coincides with the four molybdenite ages ranging from 60.0 to 60.8 ± 0.3 Ma, which were taken from that porphyry. The coincidence between the U-Pb ages for the mineralizing stocks and the mineralization and alteration ages supports the idea that different mineralization and alteration ages do in fact represent multiple, superimposed hydrothermal events.

**Implications for the genesis of Sierrita and the Pima District**

The new high-quality ages allow for a meaningful evaluation of the genetic relationships between the intrusive rocks at Sierrita, namely if they are comagmatic. To be comagmatic the magmas that crystallized to form the stocks must have been derived from the same continuously molten body at depth, i.e. the same magma chamber. Published thermal models estimate the maximum crystallization times of magma bodies in the crust to be at most one to two m.y. (Norton and Knight, 1977; Cathles, 1981; Norton, 1982; Barton and Hanson, 1989). Significantly prolonging the life of a magma chamber through recharge has been shown to be unlikely (Barton and Hanson, 1989).

These thermal constraints would suggest that the 7-8 m.y. magmatic history at Sierrita likely represents distinct, not comagmatic episodes. Rock units that did crystallize within a million-year period, on the other hand, may be comagmatic. It appears then that the diorite was sourced from a batch of magma, which crystallized and cooled before a second magma gave rise to the Ruby Star granodiorite. The quartz monzonite porphyry is plausibly cogenetic with the Ruby Star granodiorite, an interpretation supported by field evidence, namely the gradational contact between the two north of the mine. The 3 m.y. years separating the quartz monzonite porphyry from the granite porphyry and
quartz latite porphyry require that the latest two units have their origins in a third, discrete magma batch. Because 3 m.y. is adequate time for cooling of the system, hydrothermal systems associated with each of these igneous events must have been discrete systems, as well. This is consistent with recent studies of the duration of hydrothermal systems (Arribas et al., 1995; Marsh et al., 1997), but is inconsistent with published field relationships at Sierrita, because high-temperature hydrothermal mineral assemblages from the granite porphyry should be seen cutting low-temperature assemblages from the quartz monzonite porphyry.

These multiple yet separate igneous episodes were important to the formation of the Sierrita porphyry copper deposit because at least two of them were associated with mineralizing hydrothermal systems. This superposition of multiple igneous and hydrothermal events may be crucial to the formation of these deposits in general. Furthermore the discrimination of separate magma batches could allow the mineralization-related magma batches at Sierrita to be compared with those of other porphyry copper deposits, for example, in size or absolute age.

When comparing the absolute ages of the mineralization-related magmatism at Sierrita (63.4 and 60.5 Ma) to Re-Os mineralization ages at other porphyry coppers in Arizona, it appears that they do not fall into the regional mineralization intervals of 60-55 or 74-70 Ma as defined by McCandless and Ruiz (1993). These authors do, however, state that an older ~64 Ma interval of regional mineralization may exist, based on K-Ar dating of gangue minerals at Sierrita and other porphyries, although the evidence precludes certainty. A province-wide mineralization interval—irrespective of time of
onset or duration of magmatism at various deposits—would suggest a regional crustal or tectonic control on porphyry mineralization.

**Conclusion**

The new U-Pb geochronology yields the most accurate and precise crystallization ages of intrusions at the Sierrita-Esperanza deposit. The accuracy and precision of these ages allows for a better estimate of the true duration of magmatism and of the time elapsed between intrusions. There appear to have been three episodes of magmatism over 7-8 m.y., separated by 2 quiescent periods of 2-3 m.y. Some K-Ar ages of intrusion are most likely cooling ages or the result of resetting by thermal activity. The oldest K-Ar ages of hydrothermal alteration related to the main porphyry but older than its K-Ar age “correlate” with the U-Pb age of the porphyry. Re-Os ages on molybdenite taken from the quartz monzonite porphyry and the granite porphyry also “correlate” with the U-Pb ages of the respective porphyries.

The U-Pb ages allow the plausible genetic relationships between the intrusions to be evaluated. Combining geochronologic and thermal constraints, one can conclude that all magmatism at Sierrita is not comagmatic. Intrusions, however, that are separated by less than one m.y., such as the Ruby Star granodiorite and the quartz monzonite porphyry, probably are comagmatic. This implies that mineralization associated with the quartz monzonite porphyry and the granite porphyry represents two separate and superposed hydrothermal systems. Finally, the U-Pb ages of mineralization-related magmatism at Sierrita do not appear to be consistent with regional mineralization intervals identified by Re-Os geochronology.
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