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THE GEOLOGIC HISTORY OF OXIDATION AND SUPERGENE ENRICHMENT IN THE PORPHYRY COPPER DEPOSITS OF SOUTHWESTERN NORTH AMERICA

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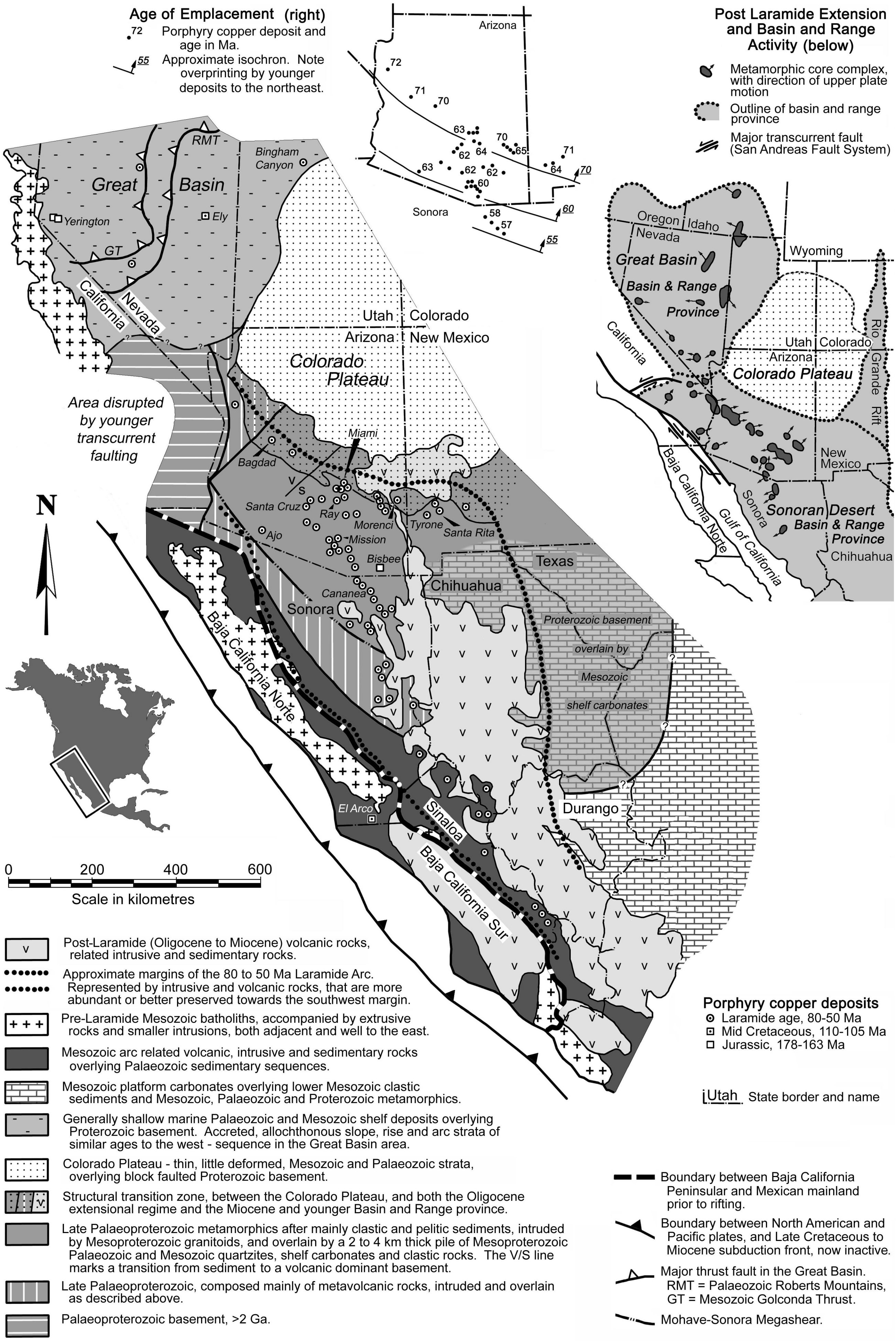
Abstract - More than fifty significant porphyry copper deposits are distributed over a 2000 km interval within the U.S. and Mexico, following a trend subparallel to the southwestern margin of North America. These include giant supergene enriched deposits such as those at Morenci in Arizona (4.7 Gt @ 0.52% Cu) and Cananea (7.1 Gt @ 0.42% Cu) in Sonora, Mexico.

The porphyry copper deposits of southwestern North America were developed in a continental margin cratonic setting, above a subduction zone that was active largely from the Early Mesozoic to the Late-Tertiary. While significant ore deposits of Jurassic to Mid-Tertiary age are known, the majority were emplaced between 72 and 55 Ma, during the peak of magmatic activity along the Laramide Arc. Laramide magmatism and crustal shortening ceased by around 50 Ma, in the mid Eocene, to be followed by a 15 m.y. period of magmatic quiescence, erosion and localised continental sedimentation, the Eocene Epeirogeny. This was succeeded from around 35 Ma by the Mid-Tertiary Orogeny, which persisted through the Oligocene to the Early Miocene and resulted in renewed, widespread volcanism, and by crustal extension. Extension was characterised by the development of listric, detachment and strike-slip faults, associated listric tilting of up to 60° or more, and the uplift and exposure of metamorphic core complexes. During the Mid- to Late-Miocene, between 18 and 10 Ma, the nature of tectonism in the region changed through a period of transition, from an extensional to a block faulted 'basin and range' regime which persists locally to the present. The typical basins are grabens or half grabens, with structural relief between the base of sediment filled basins and the crests of the adjacent ranges of from 2 to 4 km, and sometimes more than 6 km.

The majority of porphyry copper deposits in southwestern North America have undergone supergene enrichment. At many, enriched sulphide blankets constitute the principal ores exploited. Most porphyry copper deposits in Arizona and New Mexico in particular, have been subjected to multiple episodes of supergene alteration. These episodes correspond to the periods during which sulphide minerals have been present in the zone of oxidation, and reflect the common tectonic history of repeated uplift, erosion and burial which all of the deposits share to varying degrees. Supergene processes are essentially the result of a form of chemical weathering. Consequently, each episode correlates with an erosional surface, and corresponds, in a broad sense, with one of a series of time-transgressive regional unconformities separating the Tertiary tectono-stratigraphic units defined in the region. Evidence of these episodes of supergene activity, has been found in stratigraphic relationships, supported by K/Ar dating of supergene minerals. The earliest affected the Jurassic Bisbee deposit in the Early Cretaceous. Subsequent contemporaneous supergene activity occurred during the: i) Eocene at Santa Rita, Tyrone, San Manuel (and Kalamazoo), Inspiration, Sacaton and Ajo; ii) Late Oligocene to Middle Miocene at Santa Rita, Tyrone, Red Mountain, Pinto Valley, Lakeshore and Silver Bell; and iii) Late Miocene to Pliocene at Tyrone, Morenci, Bisbee, San Manuel, Pinto Valley, San Xavier North, Silver Bell and Ajo.

The geologic and tectonic setting of each of these deposits, and their hypogene and supergene mineralisation are described herein, and with the support of 22 new K/Ar dates of supergene minerals, the observations listed above are derived.


Age of Emplacement (right)
72 Porphyry copper deposit and age in Ma.
55 Approximate isochron. Note overprinting by younger deposits to the northeast.
Arizona
Sonora
Post Laramide Extension and Basin and Range Activity (below)
Metamorphic core complex, with direction of upper plate motion
Outline of basin and range province
Major transcurrent fault (San Andreas Fault System)
Oregon
Idaho
Nevada
Wyoming
Great Basin
Basin & Range Province
California
Utah
Colorado
Colorado Plateau
Rio Grande Rift
New Mexico
Baja California Norte
Gulf of California
Sonoran Desert Basin & Range Province
Chihuahua
RMT
Bingham Canyon
Great Basin
Yerington
Ely
GT
Arizona
New Mexico
Colorado Plateau
Area disrupted by younger transcurrent faulting
Miami
Bagdad
V
S
Santa Cruz
Ray
Morenci
Tyrone
Santa Rita
Ajo
Mission
Bisbee
Texas
Chihuahua
Cananea
Proterozoic basement overlain by Mesozoic shelf carbonates
N
Baja California Norte
El Arco
Sinaloa
Durango
Baja California Sur
0 200 400 600
Scale in kilometres
Post-Laramide (Oligocene to Miocene) volcanic rocks, related intrusive and sedimentary rocks.
Approximate margins of the 80 to 50 Ma Laramide Arc. Represented by intrusive and volcanic rocks, that are more abundant or better preserved towards the southwest margin.
Pre-Laramide Mesozoic batholiths, accompanied by extrusive rocks and smaller intrusions, both adjacent and well to the east.
Mesozoic arc related volcanic, intrusive and sedimentary rocks overlying Palaeozoic sedimentary sequences.
Mesozoic platform carbonates overlying lower Mesozoic clastic sediments and Mesozoic, Palaeozoic and Proterozoic metamorphics.
Generally shallow marine Palaeozoic and Mesozoic shelf deposits overlying Proterozoic basement. Accreted, allochthonous slope, rise and arc strata of similar ages to the west - sequence in the Great Basin area.
Colorado Plateau - thin, little deformed, Mesozoic and Palaeozoic strata, overlying block faulted Proterozoic basement.
Structural transition zone, between the Colorado Plateau, and both the Oligocene extensional regime and the Miocene and younger Basin and Range province.
Late Palaeoproterozoic metamorphics after mainly clastic and pelitic sediments, intruded by Mesoproterozoic granitoids, and overlain by a 2 to 4 km thick pile of Mesoproterozoic Palaeozoic and Mesozoic quartzites, shelf carbonates and clastic rocks. The V/S line marks a transition from sediment to a volcanic dominant basement.
Late Palaeoproterozoic, composed mainly of metavolcanic rocks, intruded and overlain as described above.
Palaeoproterozoic basement, >2 Ga.
Porphyry copper deposits
Laramide age, 80-50 Ma
Mid Cretaceous, 110-105 Ma
Jurassic, 178-163 Ma
Utah State border and name
Boundary between Baja California Peninsular and Mexican mainland prior to rifting.
Boundary between North American and Pacific plates, and Late Cretaceous to Miocene subduction front, now inactive.
Major thrust fault in the Great Basin. RMT = Palaeozoic Roberts Mountains, GT = Mesozoic Golconda Thrust.
Mohave-Sonora Megashear.

Introduction

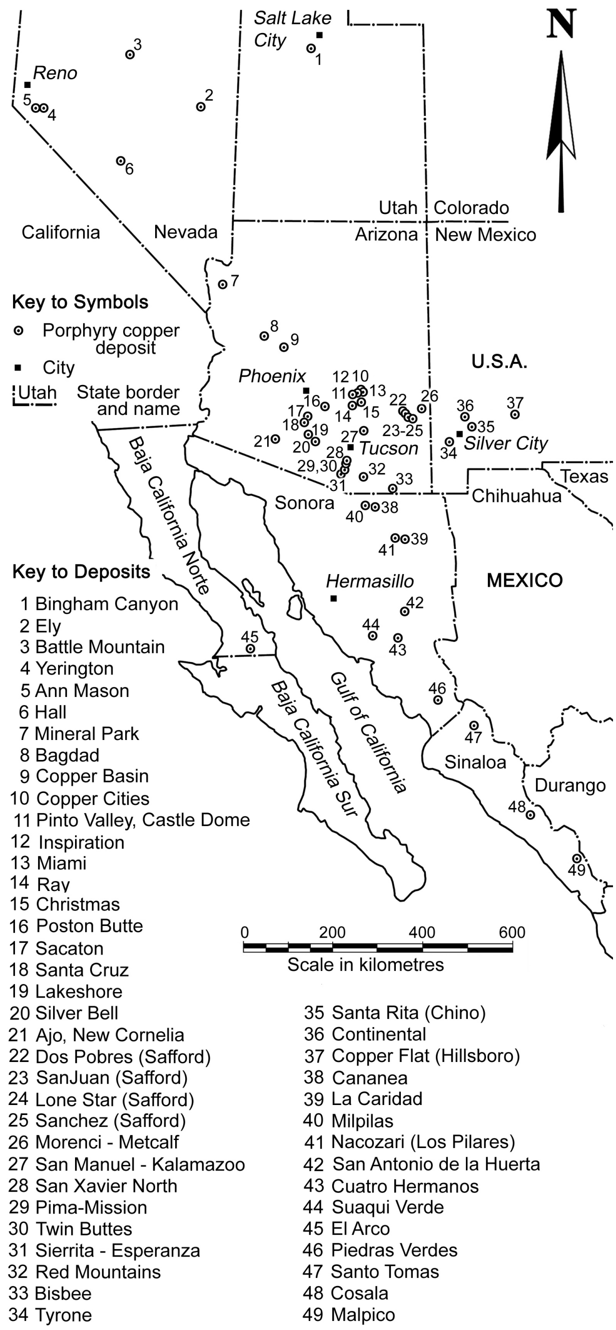
There are over fifty named and developed porphyry copper deposit in southwestern North America, extending over a generally southeast trending interval of more than 2000 km. Of these, over thirty have been commercially exploited. This belt of deposits extends through Nevada, Arizona and New Mexico in the United States, to Sonora, Baja California Norte and Sinaloa in Mexico. Porphyry copper deposits were developed in a cratonic setting along a continental margin, above a subduction zone that was active largely from the Early Mesozoic to the Late-Tertiary. While significant ore deposits are known from the Jurassic to the Middle Tertiary, the majority were emplaced between 72 to 55 Ma, at the peak of development of the Laramide Arc which lasted from 80 to 50 Ma (Titley 1993, 1995; Barton *et al.,* 1995; Wilkins and Heidrick 1995).

The formation, weathering and supergene enrichment of most porphyry copper deposits in southwestern North America occurred in an environment of uplift and volcanism (the Laramide Orogen); followed by a period of magmatic quiescence, structural adjustment and continental sedimentation (the Eocene epeirogeny); renewed volcanism and regional extension (the Mid-Tertiary orogeny); and finally, basin subsidence, uplift of intervening ranges and continental sedimentation (the Late-Cenozoic Basin and Range uplift).

Figure 1 (facing page)**: *Diagrammatic summary of the tectonic setting and age distribution of the porphyry copper deposits of southwestern North America.*** The main plan is an amalgamation of information from diagrams in Titley (1993), Titley (1995), Barton *et al.,* (1995), Wilkins and Heidrik (1995), Oldow *et al.,* (1989), de Cserna, 1989, and others cited in these references. It is a reconstruction prior to the opening of the Gulf of California. The age distribution inset (*top centre*) is after Titley 1993 and shows the main deposits in southwest US and northern Mexico, and the K/Ar age of the closest related intrusion or mineralised event. The *upper right* inset illustrates the Oligocene to Early Miocene extensional regime, the main axis of which is marked by a string of metamorphic core complexes. From Mid Miocene, the tectonic setting was dominated by 'basin and range' faulting, overlapping with the area of earlier extension. This latter activity occupied two main provinces, the Great Basin and Sonoran Desert Basin and Range Provinces, but was also responsible for the development of the Rio Grande Rift. These zones partially surround the more stable Colorado Plateau. This inset is based on a diagram in Oldow *et al.,* (1989).

Figure 2 (right)**: *Location plan showing a selection of the key porphyry copper deposits of southwestern North America.*** See Table 1 for resource/reserve + production tonnage and grade figures, and Fig. 1 for their tectonic setting. Based on diagrams in Titley (1982), Titley (1993), Wilkins and Heidrick (1995) and Barton *et al.,* (1995).

Most porphyry copper deposits in Arizona and New Mexico in the U.S., and Sonora in adjacent northern Mexico, have been subjected to multiple episodes of supergene activity. The main purpose of this paper is to record the episodes recognised in the geological history of individual deposits and districts, and to indicate that each of these episodes of supergene activity may be placed in the overall context of regional tectonic evolution.



Editors Note: Southwestern North America has been one of the world's most important porphyry copper provinces for more than a century. Supergene enrichment has played a crucial role in the economic viability of many of the porphyry deposits within the region, including some of the largest and most significant examples. Consequently the supergene history of the region is of particular pertinence to this volume.

Oxidation and supergene enrichment were critical to the commercial development of porphyry copper deposits in the region during the first half of the twentieth century, particularly those in Arizona and New Mexico. This was due to the two to ten times enrichment of hypogene copper grades within 'supergene copper sulphide' ores, commonly to greater than 1% Cu, while associated 'oxide copper' ores could often be smelted directly (Parsons 1933; Titley and Marozas, 1995). The term 'oxide copper' is used in the mines of Arizona and New Mexico in reference to ores consisting of copper silicates, carbonates, sulphates, oxides and hydroxides that contain little or no sulphides.

During the last quarter of the twentieth century, to the present, supergene enriched copper sulphide ores have remained the principal exploited resource in many porphyry copper districts in the southwestern United States and adjacent northern Mexico, although oxide ores had declined in importance (Titley and Marozas 1995). The current interest has been prompted by the amenability of most supergene copper sulphide ores to low cost and low environmental impact modern leaching and solvent extraction processing (Titley and Marozas 1995).

This paper is based on investigations undertaken and reported in a thesis submitted by the principal author (SSC) in 1995, in partial fulfilment of the degree of Doctor of Philosophy at the University of Arizona, Tucson. The study traced the post-Laramide geologic history of supergene enrichment in porphyry copper deposits from fourteen mining districts in Arizona and New Mexico. The method employed was first to study the general geology of each deposit or district, either by detailed mapping and core logging, or by careful examination of published and unpublished geologic data. The observations from this work were verified by field reconnaissance conducted, where possible, with geologists familiar with the area. The purpose of this work was to place episodes of supergene activity within the framework of local geologic history. Collation of the geologic histories from many deposits revealed possible regional correlation of episodes of supergene activity. These correlations were then tested with K/Ar dating of supergene minerals, resulting in twenty two new K/Ar dates as presented in Table 2.

The paper also outlines the tectonic and geological setting of the region, and the geology hypogene mineralisation and alteration at each deposit or district to provide a context to the supergene enrichment history. The inclusion of this information, which was summarised from available published literature, was the responsibility of the co-author (TMP).

Table 1: ***Resource/reserve and production statistics (total tonnage and grade) for selected porphyry copper deposits in southwestern North America.*** For locations see Fig. 2.

Deposit	Location	Production + Resource / Reserve	Source
Ajo - New Cornelia	Arizona, USA	742 Mt @ 0.58% Cu, 0.178 g/t Au	Mutschler *et al.,* 2004
Bagdad	Arizona, USA	1596 Mt @ 0.40% Cu, 0.01% Mo	Mutschler *et al.,* 2004
Bisbee / Warren District	Arizona, USA	605 Mt @ 0.90% Cu, 0.132 g/t Au	Mutschler *et al.,* 2004
Cananea	Sonora, Mexico	7143 Mt @ 0.42% Cu, 0.01% Mo	Mutschler *et al.,* 2004
Central District incl. Santa Rita (Chino)	New Mexico, USA	1406 Mt @ 0.62% Cu, 0.01% Mo, 0.011 g/t Au	Mutschler *et al.,* 2004
Christmas	Arizona, USA	244 Mt @ 0.46% Cu	Mutschler *et al.,* 2004
Continental	New Mexico, USA	297 Mt @ 0.65% Cu, 0.017 g/t Au	Mutschler *et al.,* 2004
Copper Basin	Arizona, USA	228 Mt @ 0.40% Cu, 0.01% Mo	Mutschler *et al.,* 2004
Copper Cities	Arizona, USA	Included in Miami - Inspiration (see below)	
Cosala	Sinaloa, Mexico	>20 Mt @ 3.7% Cu, 20% Zn, 12% Pb, 3 g/t Au, 1230 g/t Ag (skarn)	Barton *et al.,* 1995
Cuatro Hermanos	Sonora, Mexico	233 Mt @ 0.43% Cu	Mutschler *et al.,* 2004
El Arco	Baja Calif., Mexico	660 Mt @ 0.6% Cu, 0.3 g/t Au	Barton *et al.,* 1995
Ely / Robinson District	Nevada, USA	750 Mt @ 0.61% Cu, 0.272 g/t Au, 0.01% Mo	Mutschler *et al.,* 2004
La Caridad	Sonora, Mexico	1800 Mt @ 0.45% Cu, 0.02% Mo	Mutschler *et al.,* 2004
Lakeshore	Arizona, USA	446 Mt @ 0.77% Cu	Mutschler *et al.,* 2004
Malpico	Sinaloa, Mexico	<10 Mt @ 0.9% Cu	Barton *et al.,* 1995
Miami - Inspiration plus	Arizona, USA	1594 Mt @ 0.64% Cu	Mutschler *et al.,* 2004
Milpilas	Sonora, Mexico	230 Mt @ 0.85% Cu	Mutschler *et al.,* 2004
Mineral Park	Arizona, USA	171 Mt @ 0.46% Cu, 0.03% Mo, 0.027 g/t Au	Mutschler *et al.,* 2004
Morenci	Arizona, USA	4693 Mt @ 0.52% Cu	Mutschler *et al.,* 2004
Nacozari (Los Pilares)	Sonora, Mexico	147 Mt @ 1.04% Cu	Mutschler *et al.,* 2004
Piedras Verdes	Sonora, Mexico	287 Mt @ 0.37% Cu	Mutschler *et al.,* 2004
Pima - Mission+Twin Buttes	Arizona, USA	1902 Mt @ 0.69% Cu	Mutschler *et al.,* 2004
Pinto Valley (Castle Dome)	Arizona, USA	1371 Mt @ 0.32% Cu	Mutschler *et al.,* 2004
Poston Butte (Florence)	Arizona, USA	726 Mt @ 0.39% Cu	Mutschler *et al.,* 2004
Ray	Arizona, USA	1583 Mt @ 0.68% Cu	Mutschler *et al.,* 2004
Red Mountain	Arizona, USA	570 Mt @ 0.63% Cu	Mutschler *et al.,* 2004
Safford - Dos Pobres, San Juan, Lone Star, Sanchez,	Arizona, USA	7891 Mt @ 0.49% Cu, 0.016 g/t Au	Mutschler *et al.,* 2004
San Antonio de la Huerta	Sonora, Mexico	11 to 15 Mt @ 0.8 to 1.0% Cu	Barton *et al.,* 1995
San Manuel - Kalamazoo	Arizona, USA	1386 Mt @ 0.60% Cu, 0.017 g/t Au	Mutschler *et al.,* 2004
Santa Cruz, Sacaton	Arizona, USA	1449 Mt @ 0.59% Cu, 0.011 g/t Au	Mutschler *et al.,* 2004
Santa Rita	New Mexico, USA	See Central District	
Santo Tomas	Sinaloa, Mexico	250 Mt @ 0.45-0.52% Cu	Barton *et al.,* 1995
San Xavier North	Arizona, USA	161 Mt @ 0.53% Cu	Long, 1995
Sierrita - Esperanza	Arizona, USA	1829 Mt @ 0.26% Cu, 0.02% Mo	Mutschler *et al.,* 2004
Silver Bell	Arizona, USA	267 Mt @ 0.69% Cu, 0.01% Mo	Mutschler *et al.,* 2004
Suaqui Verde	Sonora, Mexico	Supergene 2000x400 m @ 0.3-0.5% Cu	Barton *et al.,* 1995
Superior - Magma	Arizona, USA	28 Mt @ 4.62% Cu, 0.919 g/t Au	Mutschler *et al.,* 2004
Tyrone	New Mexico, USA	1048 Mt @ 0.49% Cu	Mutschler *et al.,* 2004
Yerington, Ann Mason	Nevada, USA	1561 Mt @ 0.43% Cu	Mutschler *et al.,* 2004

Previous Work

An understanding of the processes and the historic geology of supergene copper enrichment of porphyry copper deposits has been developed from studies undertaken in the southwestern U.S., Mexico, Chile and Peru since the late nineteenth century. A summary of these studies and what they have revealed is included below to provide a source of further reading and to establish a background to the main subject of this paper.

The fundamental geochemistry of the supergene enrichment process was well documented by the early 1900s (Kemp 1905; Sullivan 1905; Stokes 1906; Emmons 1917). Investigation and understanding of leached outcrops has been intensively studied in southwestern North America (Locke 1926; Weiss 1965; Blanchard 1968; Loghry 1972; Anderson 1982; Gilmour 1995; Titley and Marozas 1995 and others quoted therein).

These studies (as summarised from Titley and Marozas 1995) have shown that supergene processes commence with the onset of weathering of a porphyry system, when descending oxidised fluids of meteoric origin dominate the flow through veins and stockworks. Oxidation produces oxidised iron species and acid from pyrite, lowering the pH. In addition, oxidation of either primary or secondary copper sulphides minerals releases copper into a more soluble form. Dissolution and transport of copper is enhanced if sufficient pyrite is available to form acid and ferric ion to sustain a high oxidation state. Copper thus mobilised moves vertically or horizontally across the zone of oxidation to a usually horizontal level of contrasting redox conditions, commonly the water table, where it contributes to the formation of an enriched blanket. The enrichment blanket evolves through the precipitation of copper onto un-oxidised copper sulphides and pyrite. Chalcopyrite and bornite are preferentially attacked by this process, followed by pyrite to produce a chalcocite dominated mineralogy. Enrichment blankets generally have lateral dimensions of hundreds of metres, up to a few kilometres in the larger examples, and vary from tens, to in exceptional cases, hundreds of metres in thickness.

The zone of oxidation is uppermost, and is characterised by alteration products derived from the oxidation and leaching of sulphides and the modification of silicate minerals by reaction with low pH solutions, often with an iron rich oxide "cap" overlying the main zone of leaching. Supergene sulphide enrichment is dependent upon the presence of specific host rock compositions containing copper sulphides, most commonly as chalcopyrite and bornite, accompanied by pyrite. Ideally the host rocks should: i) be less reactive (preferably potassium-aluminium silicates rather than mafic mineral- or carbonate-rich hosts) so as to not buffer the acid solutions; ii) have a pyrite content greater than that of copper sulphides, to maintain a low pH, and iii) be sufficiently porous and permeable to both allow access of oxygen (to produce a high Eh), and facilitate the migration of fluids. Oxidation of low pyrite mineralisation and/or mineralisation in a reactive host will result in the formation of an 'oxide copper' mineralogy with little or no upgrading (Titley and Marozas 1995).

Oxidation, leaching and supergene enrichment is best developed in a hot to temperate and semi-arid climate. Uplift is required to produce and maintain a hydrological gradient, although it is essential that erosion does not outstrip the development of a thick zone of strong oxidation and leaching. Pulses of uplift will lead to cycles of supergene enrichment, whereby erosion removes oxidised and leached cappings (and other subsequently deposited cover), to expose earlier enrichment blankets. These are then oxidised and leached, to produce newer, topographically lower and generally higher grade, more mature supergene blankets at the depressed water table (Titley and Marozas 1995 and references quoted therein).

The preponderance of evidence gathered to date from the studies quoted above, leads to the conclusion that leached cappings dominated by goethite and jarosite form after the oxidation of chalcopyrite, pyrite and bornite bearing mineralisation, while those rich in hematite form after the destruction of an older chalcocite dominated mineralogy.

The cordillera of North and South America share a common link in the tectonic tempo of the Pacific Basin, although in detail, their geomorphological evolution is quite different.

South America

The historic geology of copper enrichment, and in particular the relationship between sulphide enrichment and the development of the modern landscape in Chile is the subject of a series of studies undertaken by Segerstrom (1963), Clark *et al.,* (1967), Sillitoe *et al.,* (1968), Mortimer (1973, 1977) and others. From these studies it may be concluded that supergene enrichment is generally related to erosional intervals between periods of continental sedimentation. Mortimer (1973) identified the Late-Eocene to Early Oligocene and Middle to Late Miocene as the most favourable periods of supergene sulphide enrichment in Chile. The conclusions of Sillitoe *et al.,* (1968) and Mortimer (1973) were based on stratigraphic and geomorphic data constrained by radiometric dating of volcanic marker horizons, while supergene minerals were dated directly. Subsequent publications, including Gustafson and Hunt (1975), Alpers and Brimhall (1988) and Sillitoe and McKee (1996) include K/Ar dates of supergene alunite that corroborate findings from earlier studies of enrichment chronologies in Chile. Clark *et al.,* (1990) studied the age of supergene enrichment in Peru, concluding it was essentially contemporaneous with that of northern Chile

North America

Lindgren (1905) believed that enrichment in the Morenci district occurred in what he termed "Gila Conglomerate time". More recent studies in the same district by Moolick and Durek (1966) and Langdon (1973) concluded that enrichment took place in Eocene or Miocene time, or both. Atwood (1916) investigated the relation between physiographic conditions and supergene enrichment at Butte, Montana and Bingham Canyon, Utah, and concluded that the formation of modern enriched ores commenced with the dissection of an Eocene peneplain and continued intermittently until the Pliocene.

Livingstone *et al.,* (1968) investigated the enrichment and preservation of porphyry copper deposits in Arizona and concluded that most deposits in the region were enriched prior to Mid-Tertiary volcanism. Schwartz (1953) recognised three stages of enrichment at San Manuel, Arizona and correlated these stages with the intervals between the deposition of terrestrial sediments in the district. Gilluly (1946) also noted the cyclic nature of supergene processes when he documented three stages of supergene mineralisation at Ajo, Arizona. Of these, only the older, Eocene cycle of weathering resulted in enrichment, while the younger episodes produced in situ oxidation of a protore with a low pyrite: chalcopyrite + bornite ratio with no discernable enrichment.

Paige (1922) recognised three stages of enrichment at Tyrone, New Mexico, the first of which began prior to the deposition of the Mid-Tertiary volcanic rocks. The second phase commenced when the mineralisation was again exposed after the volcanics were removed by erosion. This phase was characterised by drainage into a closed basin and was initially terminated when the deposit was drowned and then covered by the Mangas Conglomerate. The third episode commenced with the removal of the Mangas Conglomerate when the district was integrated into the Gila River drainage system. A hematitic capping was formed when the earlier supergene enriched sulphides were oxidised and bodies of exotic copper mineralisation formed to the northeast during the third stage of supergene enrichment of the main deposit.

Dating of Supergene Minerals

Three minerals were used to directly date supergene events in the study reported in this paper, alunite, jarosite and illite. Alunite dates are relatively common and well accepted as indicators of both hypogene and supergene events. The isotopic composition of sulphur from some of the alunite dated was determined as a check on the supergene origin of the mineral phases. Jarosite is dated less often and is less reliable (e.g. Alpers and Brimhall 1988 discredited jarosite dates from rocks at La Escondida). Jarosite dates have been included in the interpretations reported herein, where they are consistent with the observed chemical and paragenetic relationships, as discussed below. Illite has been used to date supergene events at Bisbee, Tyrone and Pinto Valley.

Modelling of the weathering of sulphide bearing felsic igneous rocks by Bladh (1982) indicated that jarosite should precipitate in the supergene environment before alunite in almost all circumstances. Jarosite precipitates while sulphides are dissolving and pH is low, but abruptly stops forming when all of the sulphides are exhausted. Alunite precipitation only commences when all of the sulphides have dissolved and the pH begins to rise, while illite/ muscovite begins after alunite. Alunite cuts jarosite in the samples studied and reported in this paper, while the relative ages of jarosite and alunite from both Ajo and San Xavier North reflect the suggested paragenesis.

The validity of K/Ar and $^{40}Ar/^{39}Ar$ dating techniques for supergene alunite has been rigorously tested and confirmed by Bird *et al.,* (1990) (see also Sillitoe and McKee 1996). Dates obtained are assumed to be minimum ages and closure is taken to be contemporaneous with precipitation. Details of the isotopic dilution methods for argon analysis and wet chemical analysis of potassium used in the study reported in this paper are given in Livingstone *et al.,* (1967), Damon *et al.,* (1974) and Shafiqullah *et al.,* (1980). Samples with a prefix of "X" were analysed by Geochron Laboratories in Cambridge, Massachusetts (U.S.), while all others were from the Geochronology Laboratory at the University of Arizona. All alunite and jarosite specimens were hand picked from crushed samples, with the purity and field identification being checked by X-ray diffraction and examination of polished thin sections using standard petrographic techniques.

It should be noted that two of the samples analysed, (UAKA 92-22 from Tyrone, New Mexico, and UAKA 92-57 from Pinto Valley, Arizona) comprised submicron illite. The techniques utilised to determine these dates conform to the methods developed by the late M Shafiqullah (Geochronology Laboratory, the University of Arizona) by adapting those of Glassman *et al.,* (1989). The reliability of age determinations of sub-micron illite has been questioned, and consequently the results should be treated with some caution. Never the less the ages obtained are consistent with observed field relationships, and hence are included.

Tectonic and Geologic Setting

The tectonic setting of southwestern United States and the northern half of Mexico (Fig. 1) may be broadly divided into: i). a western to southwestern region of largely Mesozoic arc related rocks overlying Palaeozoic sediments, predominantly in Mexico; ii). Precambrian basement in eastern California, Arizona and New Mexico in the U.S., and northern Sonora and much of Chihuahua in northern Mexico; iii). an eastern to northeastern series of thick Mesozoic carbonate platforms built on Early to Mid-Mesozoic clastic sequences overlying poorly understood metamorphic basement of Precambrian, Palaeozoic and Mesozoic age (Barton *et al.,* 1995).

The Precambrian block in the north of the region constitutes the southwestern margin of the Precambrian North American Craton. It has been divided into three main terranes, namely: i) a greater than 2 Ga Palaeoproterozoic block in eastern California and southern Nevada, west of a north-south boundary along the Arizona-California border; ii) a Late-Palaeoproterozoic (1.72 to 1.68 Ga) terrane dominated by clastic meta-sedimentary rocks and intruded plutons, which occupies much of Arizona, New Mexico and northern Sonora; this terrane underlies or encloses the majority of the most significant porphyry deposits of the region; it has an increased volcanic component to the northwest which has a reduced density of porphyry deposits (see Fig. 1), and iii) two separated slices of Late-Palaeoproterozoic (approximately 1.8 Ga) basement composed of meta-volcanic rocks, one to the southwest of the 1.72 to 1.68 Ga terrane, separated from it by a north-west trending structure, the Mojave-Sonora Megashear; the second to the north west of the 1.72 to 1.68 Ga terrane, across a northeast-southwest trending terrane boundary and located within northwestern Arizona and southern Nevada; this terrane only underlies or encloses a small number of porphyry copper deposits (Titley 1995 and references quoted therein).

The Precambrian terranes are overlain by a variably eroded 2 to 4 km thick sequence of Phanerozoic rocks comprising Palaeozoic platform cover, predominantly of carbonate and lesser clastic sediments, a variable thickness of Mesozoic clastic and volcanic rocks, and by Mesozoic shelf carbonate rocks to the southeast in Mexico (Titley 1995 and references quoted therein).

To the north and northeast, the Precambrian North American Craton thickened and formed a more stable, less deformed nucleus, the Colorado Plateau, characterised by Phanerozoic cratonic sediments overlying a block faulted mosaic of Proterozoic basement. Laramide magmatism and tectonism, subsequent extension, and 'basin and range' faulting fringed the Colorado Plateau to the west and southwest separated by a broad transition zone marking a gradation in structural activity (Oldow *et al.,* 1989; Christiansen and Yeats 1992; Miller *et al.,* 1989).

The southwest of North America has a complex magmatic history that dates back to at least the Mesoproterozoic and continues to the present. Economic mineral deposits are largely restricted to Late-Mesozoic to Cenozoic igneous centres related to plate convergence along the Pacific margin. Magmatic rocks intrude all parts of the region, although they are best exposed in the west. Pre-Jurassic magmatism is widely distributed, but is largely dominated by Mesoproterozoic granitoids in the Precambrian block of northwestern Mexico and southwestern U.S.. Palaeozoic intrusives are rare, with the exception of equigranular Permian granitoids (without coeval volcanics) which are widely distributed through eastern and southern Mexico, related to Atlantic convergence in eastern Mexico (Barton *et al.,* 1995).

Magmatism related to plate convergence along the Pacific margin commenced with sparse, mainly mafic, Triassic volcanic rocks which are predominantly localised in what is now the Baja California Peninsula and sections of the southwestern U.S. where significant alteration and minor porphyry copper type mineralisation is known. Arc related intrusive centres were developed over a broad interval from the Baja California Peninsular to Sonora in Mexico, extending northwards into Arizona through to eastern California and Nevada. These rocks are believed to be predominantly of Jurassic age and in the west are mainly composed of basaltic to intermediate volcanic rocks with some gabbroic to tonalitic intrusions. Further inland, centres in Arizona and Sonora comprise hornblende bearing monzodiorite to quartz monzonite to granite suites, with associated andesitic volcanic rocks. These latter centres are found in some porphyry districts such as near Cananea in Mexico and in the southwestern U.S. where they may be extensively altered and carry some porphyry style mineralisation as at Bisbee in Arizona and Yerington in Nevada (Figs. 1 and 2) (Barton *et al.,* 1995). The host intrusives at Bisbee and Yerington are in the age range 178 to 163 Ma (Titley 1981; Dilles and Wright 1988).

After a Late-Jurassic lull, vigorous magmatism was renewed in western Mexico and southwestern U.S. This magamtism is represented by metaluminous diorite-tonalite suites of the composite Mid-Cretaceous Peninsular Range and Sinaloa batholiths on the Baja California Peninsula and in Sinaloa on the adjacent east coast of the Gulf of California, which were contiguous prior to the Miocene opening of the Gulf of California. In the U.S., this same period of magmatism was represented by the continuation of the composite Peninsular Range and Sierra Nevada Batholiths. Associated volcanic rocks are only common in a few areas. These composite batholiths are the exhumed roots of an ancient volcanic arc (Barton *et al.,* 1995; Oldow *et al.,* 1989). The El Arco porphyry copper deposit (660 Mt @ 0.6% Cu, 0.3 g/t Au) in Baja California Norte is associated with a 107 Ma intrusive of this episode (Barton *et al.,* 1995) while the Ely/Robinson District deposits (750 Mt @ 0.61% Cu, 0.27 g/t Au, 0.01% Mo) in eastern Nevada are hosted by a 105 to 110 Ma quartz monzonite (Figs. 1 and 2) (Titley 1981).

Beginning at approximately 80 Ma, in the Late-Cretaceous, the axis of arc magmatism migrated approximately 200 km to the northeast to cover a broad northwest-trending swathe encompassing most of the states of Sinaloa and Sonora in Mexico and Arizona and western New Mexico in the U.S. By the beginning of the Eocene, magmatic activity, though less intense, had spread further east into Chihuahua, Durango, San Luis Potosi and Zacetecas states in Mexico. Further south magmatism was more restricted and only extended for a few hundred kilometres inland from the Pacific coast. This period of magmatism represents the 80 to 50 Ma *Laramide Arc* and was responsible for most of the porphyry type copper mineralisation in the southwestern U.S. and northern Mexico (Barton *et al.,* 1995) - see Table 1 for reserve/resource + production statistics of deposits.

Laramide igneous activity was accompanied by an ENE-WSW directed compressional tectonic regime, characterised by northwest trending basement core uplifts which were flanked by reverse and thrust faults (Davis, 1979). A prominent, contemporaneous, ENE trending brittle structural fabric was also developed over a wide area, governing the attitudes of steep fractures, faults, dykes and veins and influencing intrusive emplacement (Rehrig and Heidrick, 1972; Heidrick and Titley, 1982).

Hydrothermally altered andesitic volcanic rocks are abundant and well preserved, particularly along the eastern margin of the Laramide Arc in Mexico. Northward in Arizona and southwestern New Mexico, similar volcanics are also present. The Laramide igneous centres are predominantly intermediate (altered andesites) in composition, with subordinate dacites, and are believed to represent the eroded root zones of andesitic stratovolcanoes. The most common intrusives are hornblende- (pyroxene- and biotite-) bearing quartz diorites and granodiorites to quartz monzonites, occurring as batholiths, stocks and dyke-sill swarms. Late rhyolites and quartz-feldspar porphyries are common in many intrusive centres. Coeval volcanics are sparse in the late Laramide centres, implying that most intrusions of this stage did not vent to the surface (Barton *et al.,* 1995; Titley 1995).

The cessation of Laramide plutonism, volcanism and crustal shortening, by around 50 Ma in the Mid-Eocene, was followed by a 15 m.y. period of magmatic quiescence, erosion and continental sedimentation, the *Eocene Epeirogeny*. From approximately 35 Ma, a period of extension ensued over the area of Precambrian basement, persisting from the Oligocene to the Mid-Miocene. This phase was characterised by the development of listric, detachment and strike-slip faults, associated listric tilting, and the uplift and exposure of metamorphic core complexes. Tilting of pre-Oligocene strata (and porphyry copper deposits) by listric faulting has been measured at as much as 60°. Extension on individual detachments has been measured at from 10 to 70 km directed along axes generally oriented in a direction of 55 to 70 in Arizona and Sonora (Fig. 1). The magnitude of supracrustal hangingwall extension on individual detachments varies considerably, with representative estimates of from 65 to 150%. Extension has exposed metamorphic core complexes which are highly extended, differentially uplifted and are characterised by juxtaposed supra- and infra-crustal rocks. Each comprises footwall mylonitic gneisses developed under a ductile deformation regime, overlain above a regional, low angle, curviplanar detachment fault, by an upper plate of tilted, rotated and brittle deformed Proterozoic to Miocene units. Thermobarometric studies indicate that these core complexes have undergone vertical uplift ranging from five to several tens of kilometres (Wilkins and Heidrick, 1995).

Post Laramide magmatism was initiated at around 35 Ma, in the Oligocene, and persisted for 15 to 20 m.y. to the Early Miocene, accompanying the extensional regime described above. This magmatism and structural activity comprised the *Mid-Tertiary Orogeny*. Magmatic activity is represented by voluminous ignimbrite-dominated volcanism in the Sierra Madre Occidental, erupted from multiple centres, and coalescing to form an almost continuous volcanic pile which was up to 200 to 300 km wide and extended for over 1200 km in a southeasterly direction from the Mogollon-Datil Volcanic Field in southern Arizona and New Mexico, to central Mexico. This belt of terrestrial volcanism reflects a further overall northeastward migration of the axis of magmatism. It commenced in the west, migrated eastward and then westward again, covering much of the landscape created by the denudation of the earlier Laramide topography during the Eocene quiescence. The lower series of this volcanic pile is dominated by andesitic ignimbrites, with minor rhyolitic phases, waterlain pyroclastics, agglomerates and tuffs. It is 1000 to 1400 m thick and is regionally propylitised, hosting numerous epithermal vein type precious metal deposits. After a 10 m.y. hiatus, during which the lower series were tilted and eroded, the upper series was deposited, comprising mostly rhyolitic and rhyodacitic ignimbrites, with minor mafic lavas (Barton *et al.,* 1995; de Cserna, 1989).

During the Mid- to Late-Miocene, between 18 and 10 Ma, the nature of tectonism in the area previously occupied by the Laramide Arc changed again, from a listric extensional, to a block faulted regime which persists to the present in some areas. The change also coincided with the cessation of the intense Mid-Tertiary terrestrial volcanism and the Mid-Tertiary Orogeny. This regime, which extended from the Great Basin in Nevada and Utah, into Arizona-New Mexico and to Sonora (Fig. 1), came to be characterised by 'basin and range' tectonics. It comprises gently tilted normal-fault blocks, marked by linear ranges and intervening valleys filled by thick piles of lacustrine and fluvial sediments. The trend of these linear ranges and valleys varies from generally northeast to NNE to north-south in Nevada and Utah, to predominantly SSE in Arizona and Sonora (Christiansen and Yeats 1992).

The development of the 'basin and range' regime, particularly in Arizona, New Mexico and Sonora, occurred in two stages, both superimposed on the preceding Mid-Tertiary extension. The first, in the Mid-Miocene was a transitional stage, with continuing extension which formed broad basins, accompanied by mafic to intermediate calc-alkaline magmatism. The second stage of 'basin and range' tectonics began, or accelerated at about 13 to 10 Ma and ceased by 8 Ma in western Arizona, but continues to the present further east. To the south, in southern Sonora, the first stage had commenced at approximately 21 Ma, while the second stage ceased at around 6 Ma. The typical basins are grabens or half grabens, with structural relief between the base of the sediment filled basins and the range crests of from 2 to 4 km, sometimes as much as 6 km or more (Christiansen and Yeats 1992).

There have been three periods of porphyry copper formation, in southwestern North America, one in the Jurassic (represented by the replacement and breccia complex at Bisbee in southeastern Arizona and the Yerington deposits in Nevada), a second from 110 to 105 Ma on the Baja California Peninsular (ElArco) and in Nevada (Ely/Robinson district), and the third related to the Late-Cretaceous to Late-Eocene (80 to 50 Ma) Laramide Arc (the bulk of the porphyry deposits of southwest North America). Each period corresponded to short lived episodes of near normal convergence of the North American and Pacific plates, while dating of the Laramide deposits indicates a correlation between ore deposits and a high rate of plate convergence. The restoration of the Baja California Peninsular to its pre-rift position reveals belts of deposits grossly parallel to the palaeo-continental margin. During the Laramide Arc activity, the deposits in the southwestern U.S. were some 350 to 400 km inland of that same margin. The principal deposits in Arizona and Sonora fall within the 75 to 58 Ma age bracket, while those further south in northern Sonora are as young as 55 Ma (Titley 1993; Titley 1995, and references quoted therein). There is however an overprinting of the oldest deposits by younger systems towards the northeast in southwestern New Mexico and southeastern Arizona (see the 'Age of Emplacement' inset on Fig.1)

Structural modification and brittle-fracture deformation during Mid-Tertiary extensional tectonics produced strong brittle fracturing, particularly in the plates above detachment structures, thus enhancing permeability to facilitate movement of meteoric waters and ensuing supergene processes. The subsequent large scale uplift during the 'basin and range' regime, resulted in weathering and lowering of the water table in a series of pulses, over an extended period, promoting multiple episodes of supergene leaching and enrichment. The Mid-Tertiary extensional tectonics has also relocated many of the deposits to 'smear out' the original pattern of distribution.

Geologic History of Deposits

The geology of each of the following deposits or districts, has been studied, either by detailed mapping and core logging, or by careful examination of published and unpublished geologic data, verified by field reconnaissance conducted, where possible, with geologists familiar with the area. Fig. 2 shows the location of the principal porphyry copper deposits of southwestern U.S., including those studied, while Table 1 lists the tonnage and grade figures for a representative selection of the key deposits of the region, including those described below.

Ajo, Arizona

The general geology of the Ajo district, the westernmost of the deposits studied, has been described by Gilluly (1937 and 1946) and Dixon (1966). The structural geology of the Ajo district has been reinterpreted by Hagstrum *et al.,* (1987). Two principal suites of rocks are represented in the New Cornelia pit at Ajo, namely the pre-mineral Concentrator Volcanics and the multiphase, Late-Cretaceous to Paleocene New Cornelia Pluton, which includes the 63.0 Ma productive porphyry and intrudes the Proterozoic Cardigan Gneiss. The Concentrator Volcanics are the oldest post Cambrian rocks in the deposit area. Their exact age in not known although they are in fault contact with the Cardigan Gneiss, are intruded by the Cornelia Quartz Monzonite and are unconformably overlain by the Cenozoic Locomotive Fanglomerate. They are probably of Cretaceous age and range in composition from soft, dark-grey andesite to white, hard brittle rhyolite and comprise flows, flow breccias and tuffs. Rhyolites predominate in the mine area where the New Cornelia Pluton is represented by i) the Cornelia Quartz Monzonite, which away from the deposit is a hard, massive, grey, equigranular quartz monzonite, but in the pit is a hard, massive, porphyritic quartz monzonite which grades from a strongly silicified rock, with weak sericitisation of feldspars on the western side, to softer, porphyritic quartz monzonite with widespread sericitisation and minor clay alteration to the east; and ii) the Cornelia Quartz Diorite, which surrounds the Cornelia Quartz Monzonite in the pit and ranges from quartz diorite to diorite in composition. These porphyries are located in the apex of the New Cornelia Pluton, largely exposed to the west. Hypogene mineralisation in the intrusive phases is unconformably overlain, above an erosional surface, by an alluvial conglomerate, the 37 Ma Locomotive Fanglomerate, which is in turn overlain and interfingers with the 23.8 ±0.8 Ma andesite breccias, flows and tuffs of the Ajo Volcanics. Dips become shallower upwards through the Ajo Volcanics, suggesting they were deposited during tilting. Since the deposition of the Locomotive Fanglomerate, the Ajo deposit has been tilted by at least 60°, and possibly by as much as 120° (Dixon, 1966; Titley 1982; Hagstrum *et al.,* 1987).

The hypogene zoning pattern of the mineralised system contains an outer pyritic shell in the rhyolite, along either flank of the Cornelia Quartz Diorite. An unusual pegmatitic core to the deposit (Gilluly 1946), now mined out, hosted high grade chalcopyrite and bornite mineralisation. When inspected in 1993, the ore grade (>0.6% Cu) hypogene mineralisation was hosted by granodiorite porphyry (of the Cornelia Quartz Monzonite) with 1 to 2% sulphides, K feldspar veins, thin (<1 mm) chlorite veinlets and plagioclase altered to white mica. Chalcopyrite increases from north to south, towards the contact with the Locomotive Fanglomerate. The pre-mining mineralised outcrops at Ajo comprised an oxidised zone with malachite, chrysocolla and 'copper wad' ('oxide copper' ore) which extended below the surface to the water table. Primary chalcopyrite-bornite-pyrite mineralisation were found

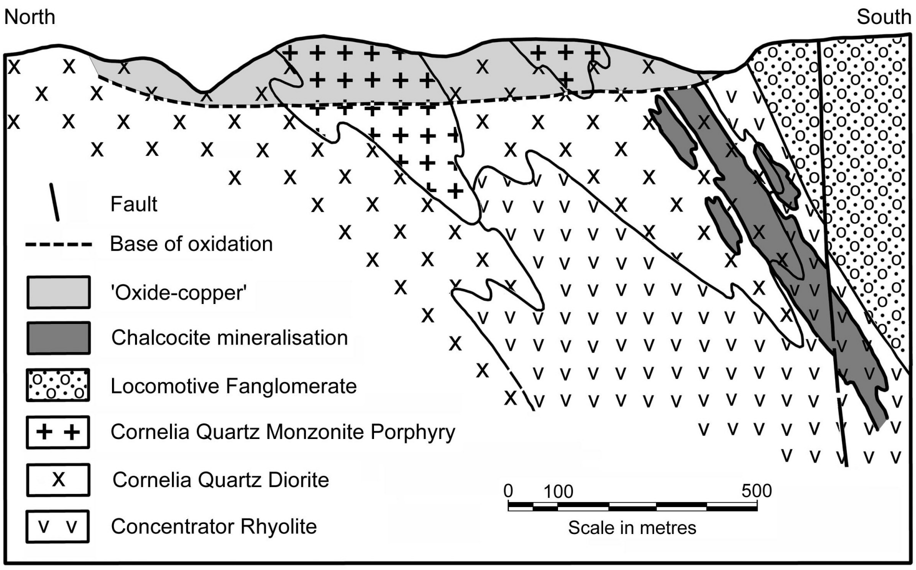


Figure 3: ***Geological cross section through the Ajo deposit, Arizona.*** The first stage chalcocite mineralisation at Ajo has been tilted steeply to the south. A second stage of weathering during late Miocene and Pliocene time caused the supergene alteration of newly exposed primary sulphides to chrysocolla, malachite and other oxide copper minerals.

immediately below the water table, except in the southern part of the deposit, where a tabular body of chalcocite and cuprite mineralisation dipped at approximately 55˚ to the south, parallel to the base of the overlying Locomotive Fanglomerate (Fig. 3) (Gilluly 1937).

The base of the Locomotive Fanglomerate is an erosional palaeo-surface. The tilted weathering profile below this surface is composed of three layers, i) a hematitic capping, ii) a thin layer of cuprite and native copper, and iii) a chalcocite enrichment blanket which has been encountered in drilling down dip to depths in excess of 600 m below the pre-mining surface. The palaeosurface on which the Locomotive Fanglomerate was deposited locally cuts through the hematitic capping and cuprite-native copper zones into the chalcocite blanket (Gilluly 1937).

It is interpreted that the deposit was exposed, weathered and enriched largely prior to the deposition of the Locomotive Fanglomerate to produce the now south dipping tabular body of chalcocite and cuprite mineralisation. Following tilting during the Mid-Tertiary Orogeny, the deposit was again exposed by erosion and a second supergene profile comprising 'oxide copper' ore, was superimposed on the tilted enrichment blanket and previously un-oxidised, low pyrite, primary mineralisation.

Table 2: ***Summary of K/Ar dating of supergene minerals from a selection of porphyry copper deposits in southwest North America***

Deposit	Sample #	Description	K_2O%	^{40}Ar pm/g	^{40}Ar*/Σ^{40}Ar(%)	Age (m.y.)
Ajo, Arizona	X-10380	Creamy white alunite from leached capping	8.629	38.386	92.00	2.6 ±0.04
Bisbee, Arizona	UAKA 92-48j	Jarosite, footwall Dividend fault	6.267	38.11	66.20	3.5 ±0.33
San Xavier North, Arizona	UAKA 92-64	Alunite from leached capping	5.915	46.64	39.90	4.54 ±0.14
Silver Bell, Arizona	X-10383	Alunite from Oxide pit, southern end of district	8.522	70.8	8.00	4.8 ±0.2
San Xavier North, Arizona	UAKA 92-65	Jarosite from boxwork cut by alunite veinlets (UAKA 92-64)	5.611	67.89	83.00	6.97 ±0.37
Morenci, Arizona	UAKA 92-05	Pale green alunite, Henessey Hill, west of Chase Creek, north of Morenci open pit	8.585	107.3	78.20	7.19 ±0.27
Tyrone, New Mexico	UAKA 92-55	Alunite	5.18	76.16	74.20	8.46 ±0.4
Bisbee, Arizona	UAKA 92-46	Alunite from Jones Hill, footwall Dividend fault	7.204	113.6	38.00	9.08 ±0.22
Morenci, Arizona	UAKA 92-21	Alunite from Standard Ridge, east of Chase Creek, northeast of Morenci open pit	8.426	144.7	69.10	9.88 ±0.26
Ajo, Arizona	X-10381	Pale yellow alunite from hematitic leached capping, western side of New Cornelia open pit	6.115	117.3	9.00	11.0 ±0.4
Silver Bell, Arizona	X-10382	Alunite from Oxide pit, southern end of district	4.462	125.5	6.00	16.2 ±0.4
Tyrone, New Mexico	UAKA 92-56	Alunite from jarositic leached capping	7.548	212.7	60.00	16.2 ±0.4
Silver Bell, Arizona	X-10607	Alunite from hematitic leached capping, North Silver Bell	4.205	119.6	2.90	16.3 ±0.5
Tyrone, New Mexico	UAKA 91-77	Alunite from Crusher fault zone	3.9328	131.8	37.60	19.2 ±0.4
Red Mountain, Arizona	UAKA 92-51	Alunite cutting veinlets with hematite boxworks after pyrite	6.514	288.1	62.40	25.3 ±0.7
Santa Rita, New Mexico	X-10606	Alunite from hematitic capping east side of Chino open pit	7.482	333.8	15.00	25.6 ±0.7
Pinto Valley, Arizona	UAKA 92-57	Submicron illite from eastern side of open pit	4.349	200.4	42.60	26.4 ±0.6
Inspiration, Arizona	X-10759	Light green alunite mixed with chrysocolla, northern end of Live Oak pit	8.12	467.5	40.00	32.9 ±0.9
Santa Rita, New Mexico	UAKA 93-11	Alunite from 5550 level, eastern side of Chino mine	8.302	498.7	49.50	34.3 ±0.9
Tyrone, New Mexico	UAKA 92-22	Submicron illite from intrusive breccia in hanging wall of Crusher fault, northern end of main pit	5.755	398.1	79.00	39.5 ±1.7
Sacaton, Arizona	X-10384	Alunite/jarosite from discovery outcrop	2.418	178.2	32.00	41.0 ±1.1
Bisbee, Arizona	UAKA 92-49	Alunite from older granite porphyry, footwall of Dividend fault	6.939	176.6	58.30	141 ±3.5

Constants: $\lambda_\beta = 1.4962 \times 10^{-10}$; $\lambda_\varepsilon = 0.581 \times 10^{-10}$; $^{40}K/K = 1.193 \times 10^{-4}$

The 'oxide copper' ore had been mined out in 1993, although sections of the tilted chalcocite blanket and overlying conglomerate contact were still exposed in the walls of the New Cornelia open pit.

Two supergene K/Ar dates (11.0 and 2.6 Ma) are available from Ajo. Both were collected from mine dumps as the surficial 'oxide copper' ore has been removed and suitable exposures could not be found in either outcrop or on the mine benches. The Late-Miocene (11.0 Ma) sample X-10381 (see Table 2), was a pale yellow jarosite from a 2 mm thick monomineralic veinlet cutting hematite rich capping in a 3 m diameter boulder of Concentrator Volcanics, which mine personnel believed to have come from the west side of the New Cornelia open pit. The Pliocene (2.6 Ma) sample X-10380, is a creamy-white alunite from leached capping, also mined from the western side of the pit. This alunite date records the exhaustion of sulphides in the weathering zone and hence the end of the second post-tilting stage of supergene mineralisation.

Formation of the now tilted enrichment blanket must have started before deposition of the Locomotive Fanglomerate, which commenced during the Late-Eocene, from at least 38 Ma (Eberly and Stanley, 1978). According to Gilluly (1937), a change from chalcocite enrichment to cuprite-rich *in situ* oxidation occurred during this period, as first pyrite-rich and then pyrite-poor primary assemblages were exposed to weathering by tilting of the deposit (see Blanchard 1968 for an explanation of the role of pyrite in supergene enrichment). Hagstrum *et al.,* (1987) cite palaeomagnetic evidence for some tilting at Ajo prior to the deposition of the Locomotive Fanglomerate, and what Gilluly (1937) observed was probably the result of this structural evolution.

The main period of tilting began during the Early Miocene and ended before 15 Ma (Hagstrum *et al.,* 1987). It follows then that supergene alteration commenced sometime before the Late-Eocene and continued until deposition of the Locomotive Fanglomerate. The K/Ar dates are evidence that suphides were oxidising again soon after tilting ended and that supergene activity continued well into the Pliocene. The pre-mining surficial zone of oxidation from this second stage showed no evidence of tilting and must be Late-Miocene or younger. On the present evidence, it is not known whether supergene activity continued at a steady state or was intermittent during the long weathering history of the deposit.

Lakeshore, Arizona

The Lakeshore hypogene copper deposit is principally hosted by the 4 km long, northwest trending, composite 67.3 ±2.2 Ma Lakeshore stock which is split into two parts by the west dipping, normal, 'basin and range' regime Lakeshore Fault (Fig. 4). The stock comprises three phases, i) equigranular granodiorite in the footwall of the Lakeshore Fault; ii) granodiorite porphyry in the hangingwall of the same fault; and iii) a biotite-quartz monzonite porphyry intruding the granodiorite porphyry. The wall rocks of the stock comprise two Proterozoic units, the Pinal Schist and the Apache Group and a sequence of Upper Cretaceous andesitic volcanic and volcaniclastic rocks. The Pinal Schist is a 1650 Ma, Late-Palaeoproterozoic unit composed of pelitic schists, which contains no commercially significant hypogene copper mineralisation in the vicinity of the Lakeshore deposit. The Mesoproterozoic Apache Group is represented in the mine area by the Mescal Limestone, Dripping Springs Quartzites and diabase (dolerite) dykes and sills which are at least 1100 Ma. Mineralisation is buried below an average of 150 m of Pliocene-Pleistocene fanglomerate, and 0 to 10 m of Quaternary alluvium. Adjacent to the Lakeshore granodiorite, the Mescal Limestone, and possibly some Palaeozoic carbonates, have been altered to a garnet and tremolite-magnetite skarn with pyrite-chalcopyrite mineralisation. The skarn bed dips at 20° W and has an average thickness of 20 m (Cook, 1988; Einaudi, 1982; Titley, 1982).

Three types of ore are recognised at Lakeshore, i) skarn ore within the Mescal Limestone (as described above) associated with weak hypogene, porphyry style, disseminated and veinlet mineralisation (dated at 64.2 ± 2.1 Ma) within the stock; ii) supergene sulphide enrichment ore, comprising three varieties, namely the chalcocite, cuprite-native copper and brochantite zones; and iii) supergene 'oxide copper' ore which include the chrysocolla, copper-wad and goethite zones. All of the mineralisation is within the hangingwall of the Lakeshore

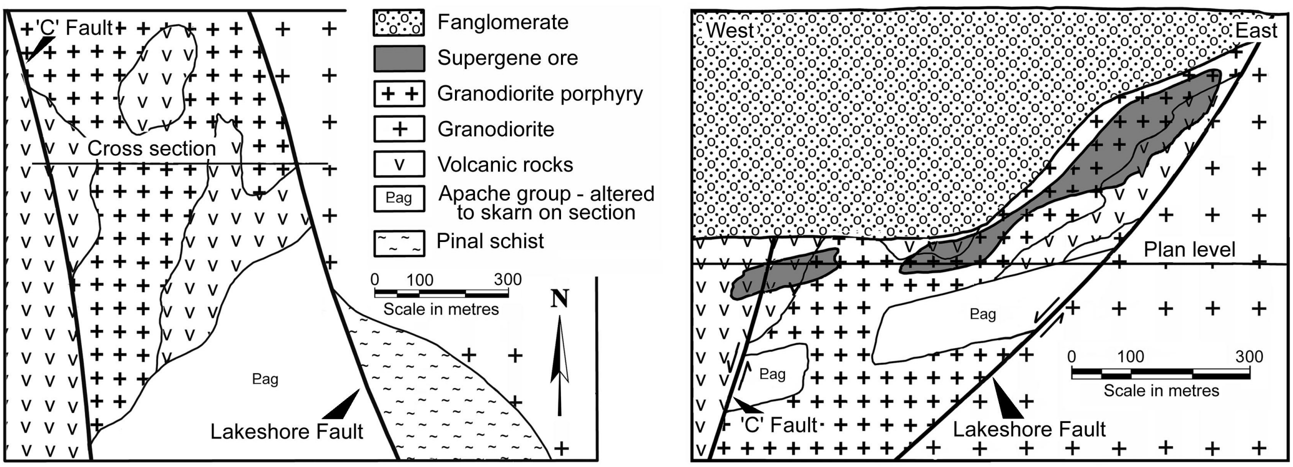


Figure 4: ***Geological cross section and level plan through the Lakeshore porphyry copper deposit, Arizona.*** After Cook (1988).

Fault, and was terminated to the east by that fault. One kilometre to the west, mineralisation is offset by the C Fault which parallels the Lakeshore Fault, and is buried by, but does not offset the fanglomerates. The C Fault downthrows the top of the supergene mineralisation by 150 m to the west, and is believed to have last been active in the Mid- to Late-Miocene (Cook 1988; Einaudi 1982).

The Lakeshore hypogene mineralisation is, overall, a sulphur poor system lacking a well developed pyrite-rich phyllic alteration halo. There is no leached cap, with the goethite zone occupying the equivalent position. Two distinct episodes of oxidation are interpreted. The first produced the chalcocite enrichment blanket and a large volume of chrysocolla mineralisation. The second episode largely destroyed the chalcocite blanket and formed the brochantite zone. The protore mineralisation and alteration determined the formation and location of the various supergene sulphide and oxide zones. The chalcocite and brochantite zones formed in rocks with a protore containing abundant hypogene pyrite and chalcopyrite mineralisation, while the chrysocolla zone was formed where the protore contained much less pyrite and chalcopyrite and more acid consuming silicates, such as biotite and plagioclase. Where the chrysocolla zone intersects the footwall shear, it is stained black by manganese rich ‘copper-wad’ to form the ‘copper-wad’ zone. Cuprite-native copper accumulations occur as isolated small blocks in biotite altered andesite to the west (Cook, 1988; Titley, 1982).

Little copper mobility is indicated during the deposition of the fanglomerates which cover the orebody. These conglomerates contain only trace amounts of copper, and immediately overlie the weathered goethite zone. The first period of enrichment formed the chalcocite zone and predated the C Fault which offsets the supergene sulphide zone by 150 m in the Mid- to Late-Miocene. There has been widespread *in situ* oxidation of the chalcocite zone since the Late-Miocene to form the brochantite, and cuprite-native copper zones. The chrysocolla zone is the most voluminous copper bearing phase (followed in volume by the brochantite and ‘copper-wad’ zones) and was formed in both stages of oxidation. The second stage of supergene activity, although widespread, was developed *in situ* and only resulted in alteration, with little further enrichment.

Santa Cruz, Arizona

The Santa Cruz deposit, 10 km to the southwest of Sacaton, (Fig. 5) forms a ridge of bedrock buried below 240 to 1100 m of un-indurated conglomerates. Mineralisation and alteration associated with the deposit extends over an area that is more than 11 km in length and 1.5 km in width. Its present configuration and depth of burial are mainly the result of horst and graben faulting, tilting and low angle faulting associated with the Mid-Tertiary extension and subsequent ‘basin and range’ tectonics. Apart from a small outcrop near the Sacaton mine, the deposit is covered by up to 1100 m of post-mineralisation alluvium, conglomerate, sandstone and minor volcanic rocks (Kreis, 1995).

Host rocks in and around the deposit include the Mesoproterozoic Oracle Granite (82%), dykes of Laramide biotite-quartz-feldspar porphyry of quartz monzonite composition (15%), and dykes of Proterozoic diabase (dolerite) and other rock types. The Laramide porphyry dykes and mineralisation are of Late Cretaceous age. Hypogene sulphides include chalcopyrite, pyrite and local bornite. The primary mineralisation and alteration is zoned with an innermost core, surrounded by a chalcopyrite zone and a pyritic periphery. The core and inner chalcopyrite zones have been subjected to alteration that produced an assemblage of biotite-orthoclase-quartz, while the outer chalcopyrite and pyrite zones have undergone quartz-sericite alteration (Kreis, 1995).

A complete supergene profile comprising leached capping, oxide copper zone and sulphide enrichment blanket are preserved. Normal faults on either side of the deposit cut the supergene profile and locally juxtapose an allochthonous block of Mid-Tertiary volcanic and volcaniclastic rocks (the “Whitetail Formation” on Fig. 5). These Mid-Tertiary rocks are not hydrothermally altered, but do host atacamite and chrysocolla mineralisation which extends down into the structurally underlying Laramide and pre-Laramide hosts. Copper is interpreted to have been transported into the allochthonous block by supergene solutions to form an ‘exotic’ deposit. No exotic mineralisation has however, been observed within the overlying alluvium and gravels. The main episode of enrichment is older than the faults which bound the allochthonous block of volcanic and volcaniclastic rocks, although the timing of the initial supergene activity with respect to Mid-Tertiary volcanism is uncertain. It is likely that supergene processes were active both before and after the Mid-Tertiary Orogeny, but had ceased before deposition of the alluvium and gravels.

Sacaton, Arizona

The Sacaton deposits are located under Cenozoic cover to the south of the Sacaton Mountains and are described in detail by Cummings (1982). The geological history of the Sacaton Mountains commenced with the intrusion of the Mesoproterozoic Oracle Granite Batholith into Late-Palaeoproterozoic pelitic, quartz-muscovite schists of the Pinal Schist. These were overlain by sediments of the Mesoproterozoic Apache Group and intruded by the 857 Ma Neoproterozoic Sacaton Granite. Minor remnants of Palaeozoic quartzites and carbonate rocks are evident locally. The preceding were cut by two Laramide intrusives, the Three Peaks Monzonite and Sacaton Peak Granite.

The two Sacaton ore deposits and alteration zone are confined to a 6.5 x 2.5 km and 400 to 650 m thick allochthonous structural block overlying a low angle detachment known as the ‘Basement Fault’ (Fig. 5). The footwall of this structure is composed of unaltered and unmineralised metamorphic rocks. The upper plate comprises brecciated and altered Proterozoic granites, diabase (dolerite) and dacite porphyry dykes, monzonite and quartz monzonite porphyries (both of which are assumed to be Laramide in age, but are different in character to the nearby Three Peaks Monzonite and Sacaton Peak Granite), and mixed breccias of these porphyries and Proterozoic granites (Cummings 1982).

Two periods of brecciation are recognised at Sacaton. The first is pre-mineral and is related to intrusion of the monzonite porphyries. Post-mineral brecciation is superimposed upon, and is more extensive than the earlier phase, with fracturing often being healed by supergene alteration minerals. The rocks of the upper plate have been strongly altered with biotite dominated potassic alteration of the monzonite and quartz monzonite porphyries, overprinted by quartz-sericite phyllic alteration within the porphyries and the surrounding breccias and granites. Hypogene mineralisation comprises disseminated, vein and vug fillings of pyrite, chalcopyrite and molybdenite which reach ore grade in the West orebody but are sub-economic in the East orebody. Both hypogene deposits have been subjected to supergene enrichment to produce economic chalcocite-covellite enrichment blankets with associated sericite-clay alteration. The Laramide and older rocks of the upper plate are largely concealed by thick conglomerates of the Mid-Tertiary Whitetail Conglomerate (Cummings 1982).

The East and West supergene enriched orebodies are fault offsets of the same deposit. They are separated by the north-south to northwest trending, 60°E dipping Sacaton Fault with a vertical displacement of at least 450 m. The Sacaton Fault, which was buried below 15 to 30 m of Quaternary alluvium, had no obvious expression on the modern landscape. The West orebody is from 15 to 150 m thick and is located in a horst to the west of the Sacaton Fault, while the East orebody is 60 to 120 m thick and is below a graben on the opposite side of the fault. A single small outcrop of leached capping was preserved on the peak of the horst, immediately to the south of the main open pit now developed on the West orebody. Mature supergene profiles comprising leached cappings, oxide zones and sulphide enrichment blankets are juxtaposed with un-mineralised conglomerate by the Sacaton Fault and related flat lying structures. This indicates that oxidation and sulphide enrichment predated the Mid- to Late-Miocene block faulting, as at Lakeshore and Santa Cruz. A single, Late-Eocene, 41.0 ±1.1 Ma supergene date is available from a sample of the original leached capping outcrop, identified in the field as alunite on the basis of a cream colour and light beige streak. Chemical analysis revealed the sample to have 2.48% K_2O, closer to the stoichiometry of jarosite than alunite. The specimen was not analysed for Fe or Na and its supergene origin is based on occurrence alone. It is not known whether oxidation and supergene alteration was continuous or intermittent between the Late-Eocene and the Late-Miocene. If they were, the event would have lasted from 25 to 30 m.y. There is no field evidence for any subsequent supergene enrichment and *in situ* oxidation appears to have been very limited since the last movement on the Sacaton Fault.

Silver Bell, Arizona

Mineralisation in the Silver Bell district is associated with an arcuate corridor of pyritisation some 12 km long and from 200 to 2000 m wide, which trends from near east-west at the Oxide Pit in the south, to north-south in the El Tiro pit to the north. The district is located within the Silver Bell Mountains, a tilted block bounded by the post-mineralisation Atlas Fault to the west, which brings the mineralised sequence into contact with the younger Tertiary Gila Conglomerates (Graybeal 1982).

Mineralisation in the Silver Bell district is associated with a series of Late-Cretaceous (67.1 Ma) Laramide stocks of quartz monzonite porphyry, the most important of which are the El Tiro and Imperial stocks associated with ore in the El Tiro pit (Fig. 6). These stocks intrude a sequence of Palaeozoic quartzites and shales which are overlain by Mesozoic clastic rocks, comprising arkose with lesser interbedded shales and minor conglomerate. Both the Palaeozoic and Mesozoic sediments are intruded by an up to 1000 m thick, shallow dipping, sill like body of Mesozoic dacite porphyry and an extensive mass of coarse grained alaskite. Both of these intrusions post date the Mesozoic clastic rocks and predate the mineralised stocks which were emplaced near the contact zone between the Alaskite mass to the southwest and the east dipping dacite porphyry sill to the east (Titley 1993; Graybeal 1982).

Alteration around the main El Tiro and North Silver Bell pits comprises a 12.5 km^2 zone of potassic alteration, characterised by disseminated biotite and K feldspar, with smaller cores of vein biotite plus K feldspar, centred on the Laramide intrusive stocks. This alteration is broadly coincident with an 8.5 km^2 zone of pyritisation. The potassic zone is fringed by a variably developed propylitic halo and is overprinted by smaller zones of phyllic quartz-sericite alteration.

Hypogene mineralisation occurs as disseminations and veinlets with chalcopyrite accompanying biotite rich potassic intervals, and chalcopyrite, molybdenite and pyrite associated with the K feldspar rich potassic zones, while pyrite is the dominant sulphide associated with phyllic alteration. The porphyry style mineralisation at the El Tiro

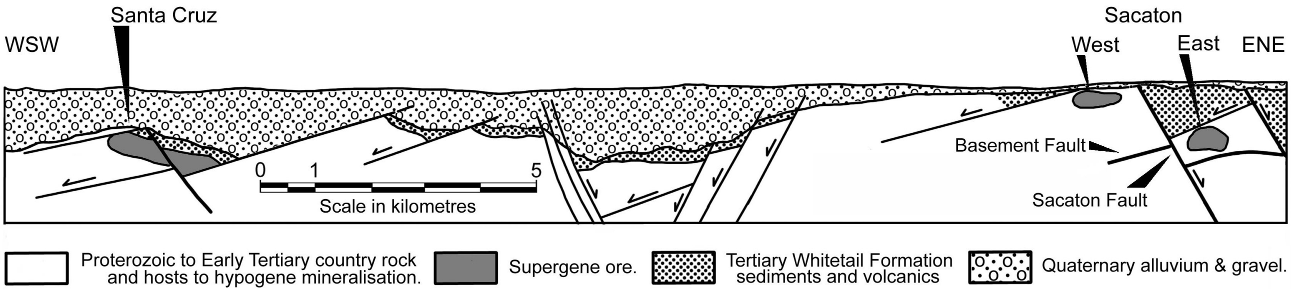


Figure 5: ***Schematic cross section extending through the Sacaton and Santa Cruz porphyry copper deposits, Arizona.*** After Wilkins and Heidrick (1995).

Pit is hosted by the porphyry stocks and alaskite, with some skarns formed from carbonate facies in the Palaeozoic sequence (Graybeal 1982). At North Silver Bell, 2.5 km to the north, the North Silver Bell Stock has invaded and mineralised the dacite porphyry. The hypogene mineralisation and alteration is very similar to that at El Tiro (Lopez and Titley, 1995).

Oxidation in the skarn "contact ores" extended to an average of 75 m below the surface, leaching sulphur and iron. No copper was transported or enriched by the meteoric waters due to the reactivity of the host. Cuprite, not malachite or azurite was the principal oxide minerals formed in the skarns of the Oxide Pit (Stewart 1912), although Graybeal (1982) reported that malachite was abundant in the skarns around the Imperial Stock.

The bulk of the ore mined from the El Tiro pit was present as a 60 m thick (using a 0.4% Cu cutoff), flat lying and tabular supergene enriched sulphide blanket overlain by a 30 m thick remnant leached capping which averaged 300 ppm Cu. The contact between the enrichment blanket and the leached capping is sharp and generally parallels the current surface. Chalcocite enrichment in the porphyries and alaskite was due to pervasive replacement of chalcopyrite and partial conversion of pyrite Copper grades within the enriched zone were relatively uniform and were not zoned relative to hypogene grades, although the copper mineralogy was strongly zoned relative to the hypogene alteration. Chalcocite dominated within zones of pyritic phyllic alteration, while chrysocolla was found, almost to the exclusion of chalcocite, in the absence of phyllic alteration (Graybeal 1982).

Prior to mining at North Silver Bell, the supergene enrichment blanket covered an area of approximately 1.5 km^2, with a tenor of around 15 metre-percent, mostly developed over altered dacite porphyry hosts. Higher grades corresponded to areas of stronger fracture density, reflecting zones of vein controlled quartz-sericite-pyrite alteration where both orthoclase-biotite and phyllic alteration were telescoped and hypogene grades were the greatest. The supergene enrichment blanket lies beneath outcropping goethite-dominant limonite capping developed by weathering and erosion of an originally thicker oxidation profile (Lopez and Titley 1995). According to Lopez and Titley (1995), the current chalcocite blanket represents a second, mature cycle of enrichment which leached an older blanket that occupied a level now marked by hematite capping exposed on ridges and slopes, overlain in turn by goethitic limonites of the older, but less mature cycle of enrichment.

Mature supergene profiles such as those at El Tiro and North Silver Bell, have been developed throughout most of the Silver Bell district and are little disturbed by faulting. Graybeal (1982) concluded that as the top of the enrichment blanket conforms to the modern surface, enrichment occurred in the modern landscape. While Graybeal (1982) noted that clasts of weakly pyritised porphyry with propylitic alteration have been found in Oligocene conglomerates east of the Oxide Pit, implying the upper portions of the orebody may have been in contact with the atmosphere then, this was not evidence of enrichment at that time. He does suggest from field evidence that the chalcocite blankets in the district formed after the emplacement of a Late-Oligocene andesite dyke.

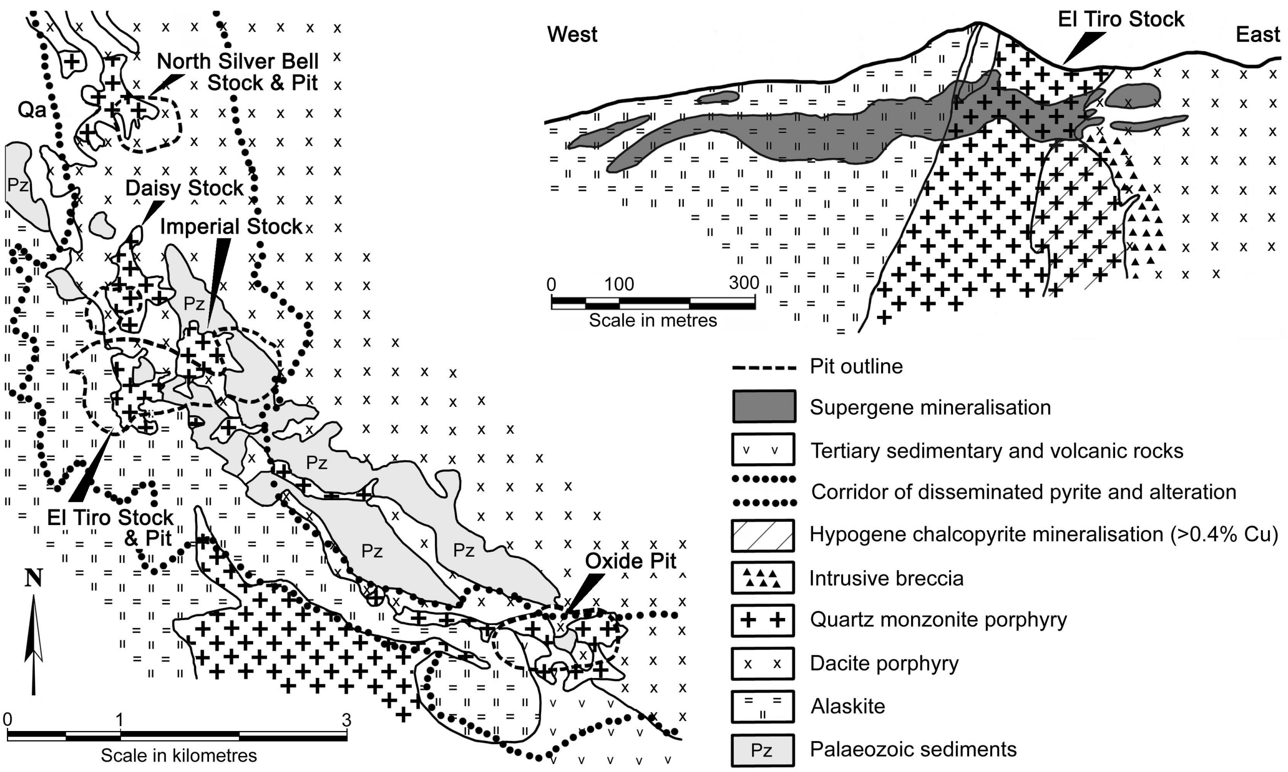


Figure 6: ***Geological map of section of the Silver Bell Complex, Arizona and cross section through the El Tiro Stock and orebodies.*** This figure is an amalgamation of information from diagrams in Graybeal (1992), Titley (1993), Lopez and Titley (1995), Cook, 1994 and others cited in these references.

By applying a copper mass balance and an estimate of the rate of erosion, Graybeal (1982) calculated that supergene enrichment had occurred over the last 3 m.y. Three supergene dates have been determined from the Silver Bell district. Two are from the Middle Miocene (16.2 ±0.4 Ma and 16.3 ±0.5 Ma), and the third is Pliocene (4.8 ±0.2 Ma). The two Middle Miocene samples were from the south and north ends of the field respectively. The 16.2 ±0.4 Ma date was obtained from alunite sample X-10382 collected on a mine bench, approximately 30 m below the modern surface, in the Oxide Pit on the southern margin of the field,. The 16.3 ±0.5 Ma alunite sample X-10607 was taken from the topographically highest, and presumably oldest leached capping preserved at North Silver Bell (S.R. Titley, pers. com.). The third date of 4.8 ±0.2 Ma from alunite sample X-10383, was collected from the mining bench some 7.5 m below sample X-10382 in the Oxide Pit. This limited set of results only indicates the time interval over which supergene leaching occurred and provides no proof of continuity, or evidence of interruption.

San Xavier North, Arizona

The San Xavier North deposit is located on the northern margin of the Pima-Mission mining district, some 2 km NNW of the Mission-Pima pit and 9.5 km NNW of the Twin Buttes pit. King (1982) has postulated that the three groups of deposits are part of the same original mineralised system which have been separated and displaced by the flat lying SanXavier Fault system during the Mid-Tertiary period of extensional tectonics. Movement on this fault is believed to have originated at around 28 Ma (Titley 1982b). The Twin Buttes deposit would represent the roots of the system, and San Xavier North the uppermost sections King (1982).

Mineralisation at San Xavier North (Fig. 7) is present in: i) 'oxide copper' zones, ii) a supergene sulphide enrichment blanket and as hypogene sulphides. All are contained within folded Cretaceous clastic sediments, predominantly gritty fine to medium grained arkosic sandstones intimately interbedded with arkosic siltstones and mudstones and occasional pebbly conglomerates. These sediments are intruded by a number of quartz monzonite porphyry dykes and a single larger mass of porphyry to the south of the pit, some of which have associated intrusive breccias. These dykes are assumed to be of the same age as the 56.7 Ma mineralised intrusions at Mision-Pima. Mineralisation is contained within both the sediments and intrusives, occurring as disseminated and fracture coatings of chalcopyrite, pyrite, molybdenite, bornite, sphalerite and galena in decreasing order of abundance. Hypogene mineralisation is zoned around a central ore zone of approximately 0.5% Cu occurring in a low total sulphide (1 to 3% sulphide) with a pyrite to chalcopyrite ratio from 1:1 to 1:3. This is surrounded by a pyrite shell with 2 to 4% total sulphide and a pyrite:chalcopyrite ratio of between 10:1 and 3:1.

The depth of weathering in the district has been shown to total around 60 m. Prior to mining, supergene mineralisation occurred as a leached capping with two oxide zones of differing character and an economically significant supergene sulphide enrichment blanket. The leached capping, 60 m of which is estimated to have been eroded, only displays minor limonite which is concentrated on the fractures, but has a high frequency of jarosite. The upper of the oxide zones occurs within the leached capping, and represents a stranded chalcocite zone which has been completely oxidised to chrysocolla in its upper sections, with lesser malachite, azurite, neotocite and melaconite, although copper carbonates increase with depth. A lower oxide zone is found immediately above the chalcocite blanket at the base of the leached capping, with a similar mineralogy as the upper zone, but with remnant supergene sulphides. The section of the supergene sulphide enrichment blanket containing significant chalcocite (i.e., ≥25% sulphide present as chalcocite) was only developed where the original hypogene mineralisation was exposed to weathering and erosion and is laterally no more extensive than the primary mineralistion immediately below. The chalcocite blanket varies from 3 to 30 m in thickness and covers an area of around 500 x 400 m (King 1982; Titley 1982).

Apart from the occurrence of two small outcrops at the time of discovery, the entire deposit is concealed by a thin sheet (<30 m thick) of Quaternary alluvium. Two stages of supergene enrichment are suggested by the presence of the lower chalcocite enrichment zone, and the oxidised hanging blanket now represented by the upper oxide zone. The upper oxide zone has been cut by the erosional surface, while the top of the lower chalcocite blanket appears to

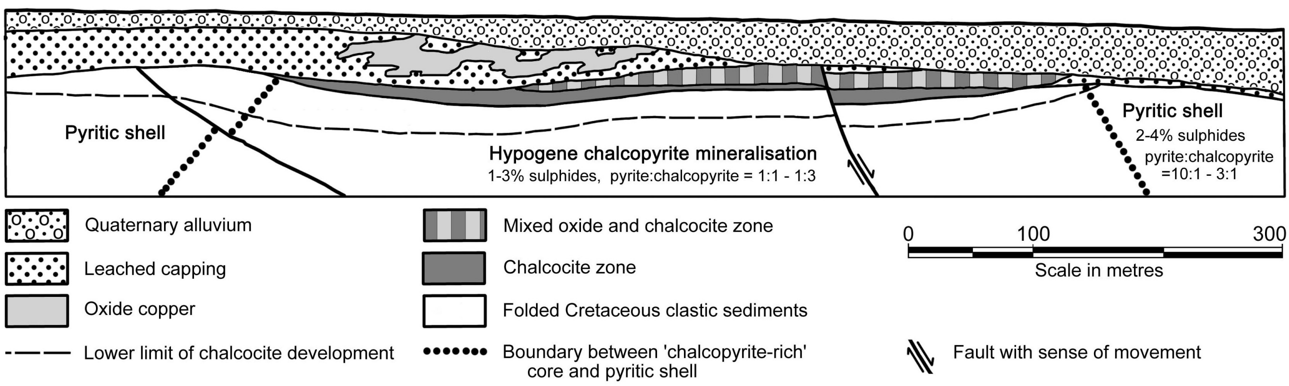


Figure 7: ***Geological cross section of the San Xavier North copper deposit, Arizona.*** After King, (1982).

have been partially truncated at the base of Quaternary alluvium. On the basis of geomorphic evidence, enrichment is believed to be quite recent. Two dates, a Late-Miocene (6.97 ±0.37 Ma - sample UAKA 92-65) and early Pliocene (4.54 ±0.14 Ma - sample UAKA 92-64) have been determined from samples collected on a mining bench in the open pit. Both samples are hand picked material from the same sample of arkose. Sample UAKA 92-65 is from a 10 mm thick jarosite vein with well developed cubic moulds (presumed to be after pyrite – see Blanchard, 1968) which cuts the arkose. Sample UAKA 92-64 was selected from a 1 mm monomineralic vein of cream coloured alunite which cuts both the arkose and the jarosite vein. The field identification and purity of both the jarosite and alunite were checked by X-ray diffraction analysis. The paragenesis of the sample, i.e., alunite after jarosite, is consistent with the predictions of Bladh (1982), and there is no reason to suspect a loss of radiogenic argon from the jarosite as suspected at La Escondida, Chile and reported by Alpers and Brimhall (1988). The Late-Miocene and early Pliocene dates are consistent with the conclusion, based on geomorphology and geological relations, that there has been recent enrichment.

Red Mountain, Arizona

Red Mountain (Fig. 8) comprises i) hypogene porphyry copper mineralisation at depths of more than 1000 m beneath surface, associated with a concealed quartz-monzonite intrusive complex of unknown size and extent; ii) hypogene enargite rich mineralisation occurring near surface, associated with pyritic phyllic and argillic alteration zones within the volcanic lithocap above the porphyry; and iii) a supergene profile and multiple chalcocite rich sulphide enrichment blankets within the near surface zone of pyrite-rich phyllic alteration (Corn, 1975; Titley, *et al.,* 1989).

The overall alteration/mineralisation system is believed to be centred on a caldera subsidence structure which was associated with explosive volcanism and sub-volcanic intrusive activity. The blind, possibly Paleocene age, intrusive breccias and monzonite to quartz-monzonite intrusions which form the core of the hydrothermal system, occur as irregular bodies, sills and dykes and are only known from deep drilling. These intrusions penetrate a strongly fractured volcanic lithocap which has been subjected to acid-sulphate and advanced argillic alteration of a dacite to rhyodacite to rhyolite tuff volcanic succession which is up to 500 m thick, overlying thick andesites and lower still, conglomerates. The underlying andesites are considered to be Late-Cretaceous to LowerTertiary in age and comprise an upper 500 m of andesites and trachy-andesites, underlain by a further 500 m of interlayered andesite, felsite and banded hornfels (Titley, *et al.,* 1989).

According to Corn (1975), both the mineralisation and alteration at Red Mountain exhibit concentric zoning patterns related to the concealed quartz monzonite porphyry intrusions. Surface exposures reflect a zonal pattern, centred on an area of phyllic alteration and Cu-Mo mineralisation that is surrounded successively by pyritic-argillic alteration and propylitic andesites. The effects of hydrothermal alteration are evident over an area with a diameter of 11 to 13 km. Vertical zoning in alteration mineralogy appears to be related to a gradual increase in sulphur and decrease in copper content from the chalcopyrite rich, low sulphur K-silicate alteration (orthoclase-biotite-anhydrite) at depth, through weak K-silicate alteration to sulphur rich phyllic and advanced argillic assemblages (silica flooded, alunite-pyrophyllite-pyrite bearing rocks) near the surface. Although not of ore grade, the near surface enargite mineralisation was a source of copper for the high level chalcocite blanket (Corn, 1975; Titley, *et al.,* 1989). Further details of alteration in the upper lithocap may be found in Bodnar and Beane (1980).

There are at least four, and possibly six, hematite rich horizons in the leached capping at Red Mountain (S.R.Titley, pers. com.). Each is the remnant of a chalcocite blanket subsequently destroyed by re-weathering (Anderson, 1982; Blanchard, 1968). The details of how uplift, climate change and basin integration have interacted during the cycles of supergene activity are not known. A supergene alunite from the uppermost (and presumably oldest) layer of hematite leached capping yielded an Oligocene (25.3 ±0.7 Ma) date. This sample was collected from a 3 mm wide, monomineralic veinlet that crosscuts quartz-sericite-limonite veinlets containing iron oxides that were clearly moulds after pyrite. It was concluded that the alunite was supergene on the basis of this field evidence alone. Deposits of iron oxide and silica-cemented conglomerate are present along drainages through the pediment on the western side of Red Mountain. The ferricrete is probably the result of Pliocene or Holocene

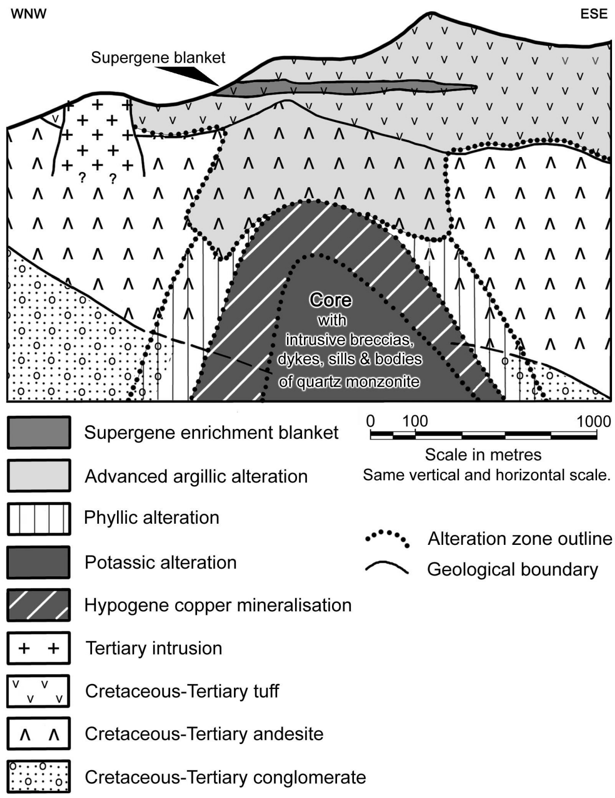


Figure 8: ***Geological sketch cross section of the Red Mountain copper deposit, Arizona.*** This figure is based on information from diagrams in Titley (1989), Corn (1975) and others cited in those references.

supergene activity, but this superposition cannot be proven from the present body of evidence.

San Manuel, Arizona

The San Manuel and Kalamazoo porphyry copper deposits (Fig. 9) are two parts of the same original orebody which have been tilted and offset by the low angle, west dipping, extensional San Manuel Fault. They lie in the footwall and hangingwall of that fault respectively. The orebodies are mainly hosted by Late Cretaceous monzonite porphyries, Mesoproterozoic quartz monzonite and minor Proterozoic diabase (dolerite) (Sandbak and Alexander 1995). Only a thin chalcocite enrichment blanket is found in the upper palaeosurface above the Kalamazoo deposit in the upper plate, while San Manuel, below the fault, contains evidence of multiple stages of enrichment and oxidation which may be correlated with erosional intervals in the Cenozoic stratigraphy of the district (Heindl, 1963; Creasey. 1967).

The hypogene ore deposits are related to Laramide age (67 to 69 Ma) monzonite (or granodiorite) porphyry intrusions which have been strongly altered over a radius of 1.5 to 2 km around the orebodies. These porphyries cut: i) the more extensive, pre-mineralisation coarse, porphyritic quartz monzonites to monzogranites of the Mesoproterozoic (1440±20 Ma) *Oracle Granite* batholith; and ii) lesser pre-ore *diabase* (dolerite), believed to be comparable in age to similar Mesoproterozoic intrusions at the Ray Mine (Sandbak and Alexander, 1995; Thomas, 1966; Lowell, 1968).

Post ore lithologies include: i) weakly mineralised and altered *igneous breccias* formed near the host monzonite-granodiorite contact and composed of altered clasts of the host intrusives; ii) *dacite porphyry*, believed to be a late Laramide intrusion, similar in composition and of similar age to the monzonite porphyry host, but darker in colour and unaltered; iii) *andesite to andesite porphyry,* believed to be Mid-Tertiary in age, occurring as sills and dykes cutting all of the previously described rocks; iv) the *Cloudburst Formation,* comprising up to 1750 m of sediments and volcanics, commencing with a 1200 to 1500 m thick lower unit of interlayered andesite to latite flows, flow breccias, tuffs and conglomerates, with related stocks; and an upper fanglomerate sequence composed predominantly of conglomerate with a muddy arkosic matrix and felsic porphyry (Laramide and Proterozoic) clasts; this unit is believed to have been deposited between 28 and 22.5 Ma; v) *rhyolite* as dykes and pods cutting the host sequence, expanding to become an extrusive ashflow tuff near the top of the Cloudburst Formation; vi) the *San Manuel Formation,* which is at least 22 m.y. old, rests disconformably on the Cloudburst Formation, and comprises red to grey conglomerates with large boulders of various intrusive rock types; it dips at 30 to 40°NE and is at least 300 m thick; vii) the *Quiburis Formation,* occurring in the San Manuel area as a Mid-Miocene to Pliocene gravel that dips gently to the NE (Sandbak and Alexander 1995).

Alteration and mineralisation are centred on the Laramide monzonite-granodiorite porphyry intrusive rocks,

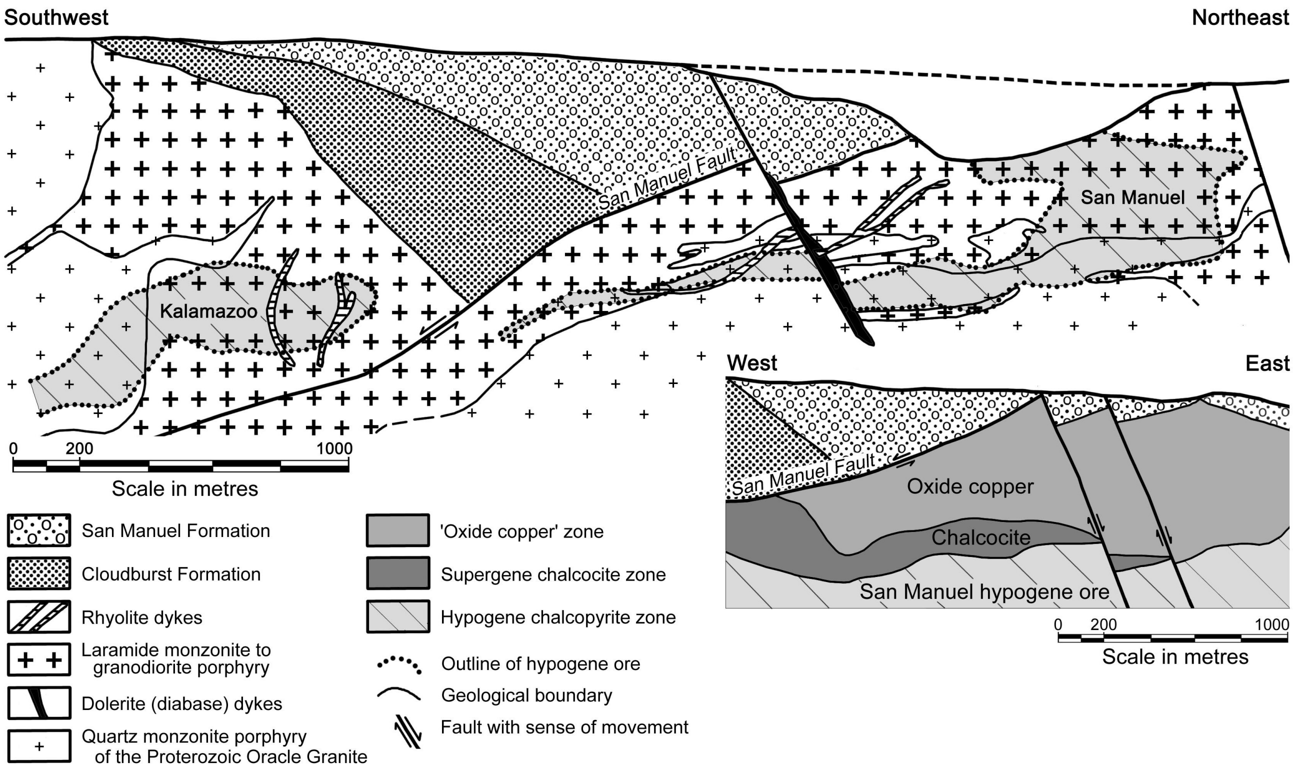


Figure 9: ***Geological cross sections illustrating the distribution of both hypogene and supergene copper mineralisation at San Manuel and Kalamazoo, Arizona.*** The *upper section*, showing the geology and hypogene mineralisation at both deposits, is based on information from a diagram in Sandbak and Alexander (1995), and others cited therein. The *lower section* is a sketch map of the distribution of supergene mineralisation prior to mining and is reproduced from a figure in Schwartz (1949).

comprising a core of potassic alteration, composed of K feldspar and biotite, surrounded by a 300 to 450 m wide phyllic zone of quartz-sericite alteration with over 10% sulphide, dominantly pyrite. The outer limits of the hydrothermal alteration/mineralisation system are defined by a propylitic halo characterised by chlorite epidote, calcite and anhydrite. The deposit has a barren core within the potassic zone with <0.3% Cu. This is surrounded by a 30 to 300 m wide ore shell developed in the potassic alteration zone, outward from the barren core, and adjacent to the contact with the surrounding phyllic alteration zone. Mineralisation in the ore shell is composed of fine disseminations and microveinlets of chalcopyrite, pyrite, molybdenite and minor bornite, totalling less than 2% sulphides, with a pyrite:chalcopyrite ratio of 2:3 (Sandbak and Alexander 1995).

The supergene zones of oxidation and enrichment at San Manuel bear no relation to the pre-mining topography or water table. They are faulted, tilted and faulted again. The effects of oxidation are seen to depths of over 400 m at the western end of the deposit, but only to around 3 m in the east. The first episode of supergene enrichment occurred in the Late-Eocene to earliest Oligocene, prior to the deposition of the Oligocene Cloudburst Formation. Supergene alteration changed from chrysocolla-rich to chalcocite-dominant during the first cycle as progressively more pyritic protore was exposed by contemporaneous tilting (Schwartz 1949). The inset on the lower right of Fig. 9, redrawn from Schwartz (1949), shows how the secondary sulphide zone pinches out between the overlying oxide and underlying hypogene sulphides, presumably as

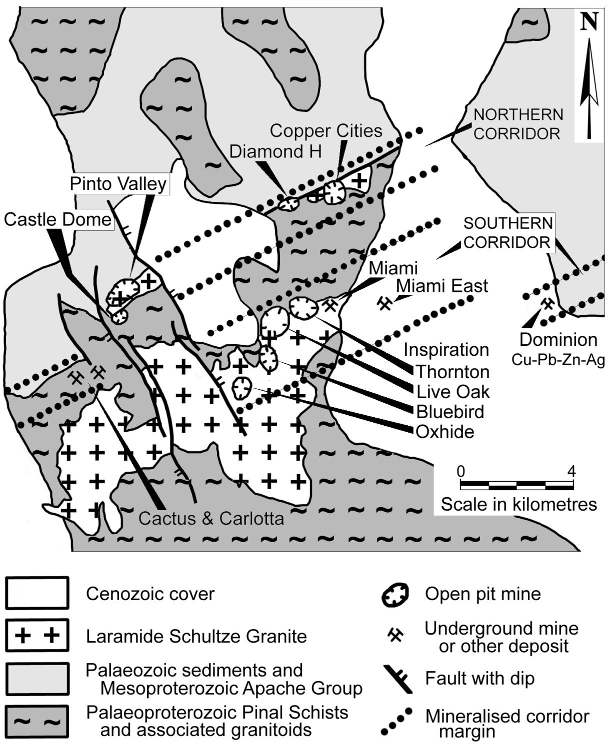


Figure 10: ***Generalised geological map of the Globe-Miami Mining District, Arizona, showing the main copper deposit.*** This figure is based on diagrams in Titley (1989), Wilkins and Heidrick (1995), Creasey (1980) and others cited in those references.

a result of tilting relative to the water table. The first cycle of supergene activity was terminated by burial beneath the Cloudburst Formation. A second episode commenced after tilting and erosion of the Cloudburst Formation and prior to the deposition of the San Manuel Formation (sometimes correlated with the Gila Conglomerate). This second stage is characterised by widespread oxidation of first stage chalcocite to chrysocolla during Miocene time and is interpreted to correlate with either the erosion surface between the Cloudburst and San Manuel Formations, or following the latter. Both supergene oxide and sulphide assemblages are largely absent at Kalamazoo. However, a thin blanket of chalcocite, with no evidence of Miocene oxidation, is found on the eastern end of the orebody below the Cloudburst Formation, where it has been tilted to an almost vertical orientation. This implies that the Kalamazoo orebody was offset from the San Manuel deposit before the second stage of supergene alteration at San Manuel.

Inspiration, Arizona

Inspiration is one of a cluster of at least fifteen separate copper deposits in the Globe-Miami district associated with an assortment of phases of the Laramide age Schultze Granite (Fig. 10). The district contains igneous, metamorphic and sedimentary rocks of Proterozoic, Palaeozoic, Tertiary and Quaternary age. The oldest are the Palaeoproterozoic pelitic and amphibolitic schists of the Pinal Schist, which are intruded by a series of Palaeoproterozoic and Mesoproterozoic granodiorite, diorite and granite bodies ranging in age from >1600 to 1400 Ma. All were eroded and overlain by the platformal conglomerates, quartzites, shales and carbonates of the Mesoproterozoic Apache Group and the succeeding Troy Quartzite. These were intruded by 1100 Ma dykes and sills of diabase (dolerite) and gabbro. Following a long break, Devonian and Carboniferous carbonates were deposited. During early Tertiary time, a large, composite quartz monzonite pluton, the Schultze Granite, was intruded over an area of several tens of square kilometres. All of the porphyry copper mineralisation at Globe-Miami is associated with this intrusive phase, although the age of individual deposits across the district spans a 5 m.y. period from 63.3 ±0.5 Ma at Copper Cities, to 59.5 ±0.3 Ma at Inspiration, and 59.1 ±0.5 Ma at Pinto Valley. Following uplift, erosion and exposure of the mineralisation, the Oligocene Whitetail Conglomerate was deposited in local basins, and was succeeded, after further deformation and erosion, by the Apache Leap Tuff, a thick sheet of Miocene ash-flow tuff. During the Basin and Range Event, coarse Pliocene conglomerates, gravels and fine grained lake deposits were laid down in local basins, followed by continued uplift, erosion and continental sedimentation (Creasy, 1980).

According to Creasey (1980) the Globe Miami district comprises a central concentration of deposits (including Inspiration), surrounded by peripheral, more isolated porphyry occurrences (which included Pinto Valley as described below) and polymetallic vein deposits. In addition, these deposits are localised along two discrete, parallel, ENE trending corridors which are some 3 to 4 kilometres apart, but have been offset by later faulting, as illustrated on Fig. 10 (Creasey, 1980; Wilkins and Heidrick, 1995).

In the Inspiration mine area, the Schultze Granite has an overall granitic texture, but includes granodiorite, quartz monzonite and porphyritic quartz monzonite. It is intruded, across a gradational boundary, by a separate, younger, marginal phase known as the Granite Porphyry, which was emplaced along its east-west trending contact with the Pinal Schists. The Granite Porphyry is the host to half of the hypogene mineralisation at Inspiration, with the remainder being within the enclosing main Schultze Granite and Pinal Schist to the south and north respectively. The distribution of the original hypogene mineralisation was influenced by structure, with the higher grades occurring along the main faults. Overall, the hypogene ore was of a low tenor (generally <0.4% Cu), and was characterised by pyrite, chalcopyrite, molybdenite and lesser bornite, and followed the emplacement of the Granite Porphyry. It was accompanied by K feldspar alteration, occurring as intense orthoclase veining, and silicification, with a strong sericite alteration overprint, and was surrounded by a halo of propylitic alteration (Olmstead and Johnson 1966).

The bulk of the ore mined at Inspiration was from the supergene sulphide enrichment blanket developed over the low grade hypogene mineralisation. The original orebody (Fig. 11) was distributed over a generally east-west trending zone some 2.5 km long and 750 m wide, following the underlying Granite Porphyry. Prior to mining, the remnant leached cap varied from 0 to 300 m in thickness. At the base of the leached capping there was a reasonably consistently developed oxide zone with a thickness averaging 60 m, developed from oxidation of the underlying supergene sulphides to form chrysocolla, malachite, azurite, minor "copper pitch", brochantite , atacamite, lindgrenite, liberthenite and very rare metatorbenite. The underlying supergene sulphide blanket varied from 60 to 150 m in thickness. The sulphide assemblage in the supergene zone was composed of chalcocite and covellite with remnant and partially replaced chalcopyrite, bornite and pyrite (Olmstead and Johnson, 1966).

The main chalcocite enrichment blanket at Inspiration was offset by Mid-Miocene or younger faulting, allowing the oxidation of sections of the chalcocite blanket to form the oxide zone described above (Anderson, 1989; Olmstead and Johnson, 1966). The sulphide enrichment must have therefore occurred during or before the Miocene, while the oxide zone developed sometime after the Mid-Miocene. A pale green alunite sample (X-10759), collected during a reconnaissance of the Live Oak Pit at Inspiration, yielded an early Oligocene K/Ar age of 32.9 ±0.9 Ma. The sample was taken from an irregular veinlet with a maximum thickness of 1 mm, cutting an exposure of Proterozoic granite. Chrysocolla was abundant in the same generation of veinlets. A mineral separate was prepared by hand picking and its purity checked by standard X-ray diffraction techniques. The K/Ar date places the beginning of supergene activity in the early Oligocene and appears to relate to the formation of the main enrichment blanket.

Pinto Valley, Arizona

The Pinto Valley porphyry copper deposit lies on the western periphery of the Globe-Miami district (see Fig. 10 and the Inspiration description above for the district setting). The deposit is almost exclusively composed of hypogene ore and lies below the old Castle Dome supergene orebody. The ore is primarily hosted by the 1400 Ma Lost Gulch Quartz Monzonite and to a lesser extent by the two phase Laramide Schultz Granite. All of these intrusives cut the Paleoproterozoic Pinal Schists, an 1100 Ma diabase (dolerite) mass and Devonian carbonates within the pit. None of these latter lithologies have been significantly mineralised, although the carbonate has been extensively altered to skarn. The annular orebody, which plunges to the north at around 45°, surrounds a barren core characterised by a high density of un-mineralised quartz veining. The orebody comprises stockwork veinlet and disseminated sulphide mineralisation, mainly chalcopyrite, associated with biotite rich potassic alteration, which are overprinted by pyritic veins with associated phyllic selvages (G. Lenze, Pers. Comm.). Hypogene mineralisation has been dated at 59.1 ±0.5 Ma (Creasy, 1980).

The Pinto Valley deposit is located in a horst, bounded to the west and east by outward dipping normal faults (Fig. 10). The uplift of the horst is believed to have kept pace with chemical weathering, although the age of that weathering is not well constrained by field evidence.

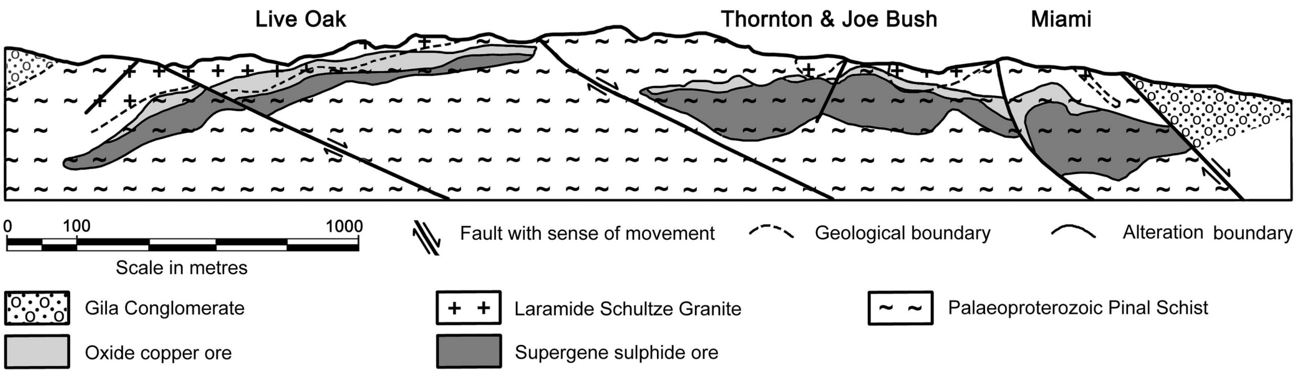


Figure 11: ***Geological long section through of the Miami-Inspiration supergene copper deposits, Arizona.*** This section is based on information from Wilkins and Heidrick (1995) and others cited in this reference.

Petersen (1962) reported that the top of the supergene mineralisation conformed closely to the pre-mine topography. Immediately to the west of Pinto Valley, in the Cactus-Carlotta copper deposit, there is evidence of at least two cycles of weathering and enrichment. The Cactus-Carlotta deposit is hosted by a breccia which is believed to be the product of a large landslide of Pinal Schist containing partially oxidised veinlets and disseminations of pyrite from the upper parts of the Pinto Valley mineralised system. The copper at Cactus-Carlotta is thought to have been introduced by supergene solutions derived from weathering of the Pinto Valley sulphide mineralisation, which percolated through the breccia and precipitated as chalcocite partially replacing the original pyrite within the breccia. These supergene sulphides were subsequently oxidised to chrysocolla and 'copper-wad' (G. Lenze, Pers. Comm.). The Cactus-Carlotta mineralisation is overlain by the Early-Miocene (ca. 17 to 20 Ma) Apache Leap Tuff. Some copper mineralisation is found in the base of the Apache Leap Tuff, indicating that at least some of the supergene mineralisation is Late Miocene.

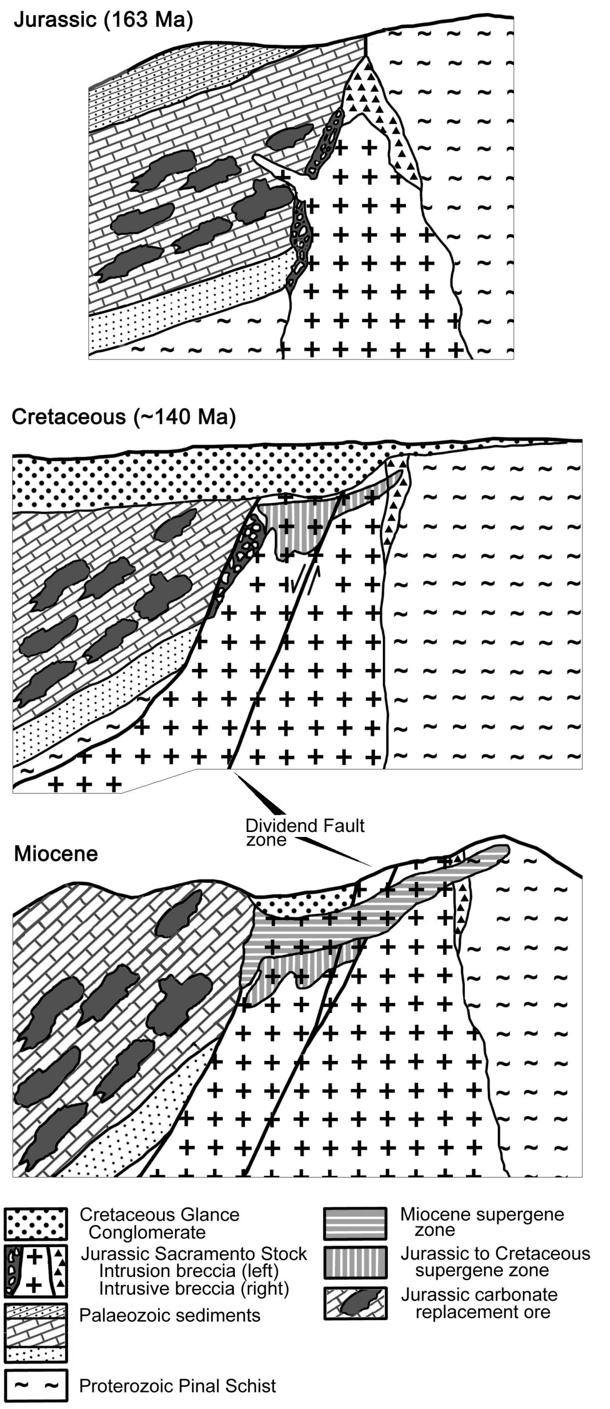


Figure 12: ***Diagrammatic cross sections illustrating the history of emplacement and supergene enrichment at Bisbee, Arizona.*** The hydrothermal hypogene porphyry copper mineralisation, and associated carbonate replacement deposits, formed during the Jurassic, with cooling finishing at around 163 Ma. The district was buried in latest Jurassic to earliest Cretaceous time by the Glance Conglomerate, the base of which contains clasts of leached capping and chalcocite mineralisation. This is evidence of at least one stage of supergene oxidation and enrichment during the Jurassic. Oxidation prior to the deposition of the Glance Conglomerate reached as deep as 900 m into the bedrock. Laramide uplift and subsequent erosion initiated renewed supergene activity which resulted in an overprinting, now dominant Miocene stage of enrichment.

Sample UAKA 92-57 of sub-micron illite from the leached cap on the eastern perimeter of the Pinto Valley pit yielded a Late-Oligocene date of 26.4 ±0.6 Ma. The sample was separated from the Proterozoic granodiorite porphyry host and is subject to the uncertainties discussed in the 'Introduction' section. The date is included here because it is possibly a record of sulphide oxidation that preceded the Cactus-Carlotta landslide. The geomorphic evidence presented above however, indicates that the chalcocite enrichment was much younger than Late-Oligocene.

Bisbee, Arizona

The Late-Jurassic Bisbee porphyry copper deposits are the oldest in the region, and consequently have the longest history of weathering and supergene enrichment. A large Jurassic granitoid body, the Juniper Flat Granite, and associated dykes intrude Proterozoic and Palaeozoic rocks in the Mule Mountains north of the township of Bisbee in the Warren district. The intruded succession includes pelitic quartz-sericite schists of the Late-Palaeoproterozoic Pinal Schist unit and Palaeozoic sediments including the Cambrian Bolsa Quartzite, which grades upwards into the 240 m thick Cambrian Abrigo Limestone. These are unconformably overlain by the up to 115 m thick Upper Devonian Martin Limestone, the 200 to 250 m thick Early-Carboniferous Escabrosa Limestone and then a sequence comprising 300 m of Late Carboniferous Horquilla Limestone, the 140 m thickness of lower clastics and upper limestones to dolomites of the Permo-Carboniferous Earp Formation, and the 80 m thick Permian Colina Limestone. No other pre Jurassic rocks appear to have been deposited in the Warren district (Bryant and Metz, 1966; Riggs *et al.,* 1994).

The Juniper Flat Granite, which has been dated at 178 to 163 Ma by K/Ar methods, forms a northwest trending elongated stock in the Mule Mountains. It grades downwards, from a fine to medium-grained phase, quenched by Pinal Schist roof rocks, through a porphyritic phase and into a lower, coarse-grained, equigranular granite. An associated, temporarily indistinguishable, highly altered and mineralised intrusive complex, the Sacramento Stock, occurs as an approximately 1.5 km diameter body, about which the known orebodies are peripherally distributed.

The Sacramento Stock complex comprises: i) an intensely silicified and pyritic quartz porphyry at the centre of the complex, possibly the oldest phase; ii) a breccia composed of an intensely silicified mixture of schist, quartzite, limestone and quartz porphyry fragments, possibly formed during the emplacement of the quartz porphyry, designated an 'intrusion breccia'; iii) a sericitised, slightly pyritic, feldspar-quartz porphyry in the eastern section of the stock; iv) a heterogenous breccia of rounded fragments of schist, quartzite, limestone, both porphyries and low grade siliceous sulphides, designated an 'intrusive breccia' (Bryant and Metz, 1966; Riggs *et al.,* 1994 and references quoted therein).

The Juniper Flat Granite and the Sacramento Stock are discordantly overlain by up to 1500 m of Lower Cretaceous Bisbee Group clastic rocks. The lowest unit of this group, the Glance Conglomerate, is composed of imperfectly rounded pebbles to boulders derived from pre-Cretaceous rocks of the Warren district, set in a reddish, fine grained matrix, and deposited on a high relief surface which varied with the basement lithologies. This unit was overlain by the 550 m thick Morita Formation shale and sandstone, in turn succeeded by the 200 m thick Mural Limestone. The top of the Bisbee Group is marked by the 550 m thick Cintura Formation shale and sandstone. The Cretaceous sequence is overlain by Quaternary and Recent fluviatile deposits.

A major WNW trending normal fault, the Dividend Fault, with south-side down movement, cuts through the ore zone, displacing the northern margin of the Sacramento Stock. All of the ore is found on the southern side of this fault. This structure is also believed to have controlled the emplacement of the Sacramento Stock. Three styles of mineralisation have been recognised, namely: i) weak, hypogene porphyry style copper mineralisation within the Sacramento Stock; ii) supergene sulphide enrichment ore developed over the Sacramento Stock; and iii) carbonate replacement ores mainly within a stratigraphic thickness of 300 m of the upper Abrigo, Martin and lower Escabrosa limestones, forming irregular bodies radiating outwards from the margins of the Sacramento Stock, south of the Dividend Fault.

The porphyry style mineralisation is best developed within the 'intrusion breccia', occurring as irregular lenses of very rich chalcopyrite and bornite, grading outwards into disseminated ore, and in adjacent sections of the feldspar quartz porphyry where disseminated mineralisation is developed. The 'intrusive breccia' has only poor hypogene sulphides, while the strongly (15 to 18%) pyritic quartz porphyry in the core of the stock contains very little primary copper. The distribution of ore in all of the phases of the Sacramento Stock is erratic. The supergene sulphide enrichment blanket was 15 to 120 m thick and dipped to the east. It had an erratic upper surface and occurred as sooty chalcocite and local covellite, developed on disseminated and fracture controlled chalcopyrite and bornite, and on sphalerite grains within the 'intrusive breccia'. The carbonate replacement ores occurred as generally irregular, cylindrical shaped bodies of from a few thousand to exceptionally more than a million tonnes, developed within the more brittle and intensely fractured facies of the host limestones. The copper ore of these carbonate replacement bodies was 'underlain' by low grade, intensely silicified and pyritised carbonates and was generally associated with either porphyry dykes and sills, or the contact of the stock adjacent to porphyry style mineralisation. They were also associated with 'intrusive breccias' within the limestones. Near surface, the carbonate replacement ores were weathered to form oxide orebodies of malachite, azurite, delafossite, cuprite, native copper and chalcocite which sustained early production within the Warren distict. No supergene sulphide enrichment is recorded in the reactive carbonate hosted ores (Bryant and Metz, 1966).

The depth of oxidation in the district is highly variable and bears no discernable relationship to the current topography or water table, but correlates closely with the base of the Glance Conglomerate. Clasts of gossan and chalcocite mineralisation are found in the basal sections of the Early-Cretaceous Glance Conglomerate, indicating that the main period of supergene activity in the replacement and the porphyry deposits took place between the Mid Jurassic and Early-Cretaceous (Bonillas, *et al.,* 1916). Oxidation had extended to depths of as much as 500 m into the bedrock by the Early-Cretaceous. Movement on the Dividend Fault during deposition of the Glance Conglomerate was at least 1000 m (Emmons, 1917), preserving the products of pre-Cretaceous supergene activity from later erosion. Subsequent Cenozoic erosion and rejuvenation of the Dividend Fault resulted in renewed supergene oxidation (Fig. 12). The chalcocite ores mined from the Lavender Pit in the Sacramento Stock are known to have extended north across the Dividend Fault. Detailed geological cross sections incorporating data from extensive exploration drilling conducted during the early 1990s show no apparent offset of the top of the supergene sulphide enrichment zone northward across the fault zone (Fig. 13), where it conforms closely with the modern topography, overlain by a thin hematite leached capping. These data indicate a very recent episode of supergene activity at Bisbee.

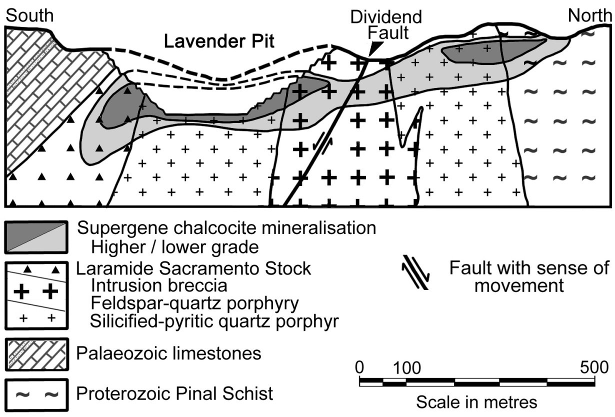


Figure 13: ***Geological cross section through of the Lavender Pit at Bisbee, Arizona.*** Chalcocite mineralisation north and south of the Lavender Fault (centre of the section) shows no offset across the structure. Alunite from the northern part of the blanket has a K/Ar age of 9 Ma, evidence that the chalcocite mined in the Lavender-Sacramento open pit reached its final form during the late Miocene, after the latest movement on the Dividend Fault.

A jarosite and an alunite sample collected from hematite leached capping north of the Dividend Fault yielded Pliocene (3.5 ±0.33 Ma) and Late-Miocene (9.08 ±0.22 Ma) ages respectively. The younger sample (UAKA 92-48) was jarosite with a well developed cubic boxwork texture (after pyrite) from a brecciated quartz vein cutting silicified granite porphyry. The sample was taken from a small test pit approximately 7.5 m below the original surface. The field identification and purity of the sample were verified by X-ray diffraction analysis. The older sample (UAKA 92-46) was alunite from a 10 to 15 mm wide, monomineralic veinlet cutting the Proterozoic granite porphyry exposed in a road bed approximately 200 m north of the Lavender Pit. The sample was from around 0.3 m below the original surface. These two dates support the conclusion that supergene processes have been active within the modern landscape at Bisbee.

Morenci, Arizona

The Morenci mining district hosts the largest supergene sulphide enrichment deposit in southwestern U.S.A. (see Table 1), and one of the largest in the world (Melchiorre and Enders, 2003).

The Morenci district is located at the transition from the Basin and Range physiographic province to the Colorado Plateau. The district is an intricately faulted plateau, covered by Cenozoic volcanic flows, that have been subsequently eroded. The geological setting comprises a basement of Proterozoic schist, quartzite, and felsic intrusives, unconformably overlain by 300 m of Palaeozoic quartzite, limestone and shale. These are succeeded by the remnants of a 250 m thick Cretaceous sequence of shale and sandstone, Laramide intrusives and then by Tertiary volcanic flows and intrusive pipes of basalt, andesite and rhyolite that encircle the district. Coarse, semi-consolidated Pliocene conglomerate is found in the south of the district (Moolick and Durek, 1966).

Within the district, the oldest Precambrian rocks are steeply dipping pelitic schists and quartzite correlated with the Palaeoproterozoic Pinal Schist unit. These metamorphics are intruded by a Proterozoic granite-granodiorite complex, comprising: i) a reddish, coarse-grained orthoclase, albite, quartz and minor biotite granite with local dykes and porphyritic phases; ii) a coarse-grained, green, granodiorite containing oligoclase-andesine and biotite with orthoclase and quartz; and iii) a possibly younger, dark grey, gabbroic facies with hornblende and some labradorite. The Proterozoic basement rocks are unconformably overlain by a Palaeozoic sequence commencing with the 50 to 75 m thick Cambrian Coronado Quartzite and followed successively by the 259 m thick Ordovician Longfellow Limestone; basal limestone and overlying shale of the 50 m thick Devonian Morenci Formation; and the 50 m thick Lower Carboniferous Modoc Limestone. Following a period of deformation and severe erosion, the Palaeozoic sequence is overlain above an angular unconformity by the Cretaceous Pinkard Formation which consists of shale and sandstone with a maximum known thickness of 250 m, now largely eroded (Moolick and Durek, 1966).

No post Proterozoic intrusive activity is recorded in the Morenci district until the commencement of Laramide magmatism at the Cretaceous to Tertiary transition, when stocks, dykes and sills of mainly porphyritic rocks were emplaced to form a northeast elongated igneous complex with dimensions of some 15 x 1 to 6.5 km. The complex was introduced during the Early-Eocene in three phases between 56 to 55 Ma, commencing with diorite, and progressively evolving to quartz monzonite and then to granite. *Diorite Porphyry* is found in the southwestern part of the intrusive complex at Morenci, mainly intruding Cretaceous shales of the Pinkard Formation and containing large phenocrysts of hornblende and labradorite. *Quartz Monzonite Porphyry* is the principal ore related phase and the most extensive of the complex. It consists of small, closely packed phenocrysts of orthoclase, albite and oligoclase in a microcrystalline groundmass of quartz and feldspar and is generally strongly altered to a light grey or white rock. *Granite Porphyry* represents several phases of emplacement with marked textural differences and intrusive contacts, and has been divided into an Older and Younger Granite Porphyry. While it is texturally similar to the Quartz Monzonite Porphyry, the younger phases of Granite Porphyry have more and larger quartz phenocrysts than the older varieties. All three also occur as dykes and sills, although the Diorite Porphyry is less frequently represented in this form. Diabase (dolerite) dykes, sills and small bosses are also present.

Local breccia pipes and sheets with long axes of up to 750 m were formed to the north of the deposit, mainly within the Granite Porphyry, in the southern sections of the Quartz Monzonite Porphyry, and adjacent Proterozoic basement (Moolick and Durek, 1966; Melchiorre and Enders, 2003).

Hypogene sulphide mineralisation at Morenci is associated with pervasive quartz-sericite-pyrite alteration of felsic host rocks, both Laramide porphyries and Proterozoic granodiorite. It carries an average of 0.1 to 0.28% Cu associated with 4 to 7 weight percent sulphides, principally pyrite (Melchiorre and Enders, 2003). Primary mineralisation is present as small veinlets and disseminations of pyrite, chalcopyrite, molybdenite, sphalerite, rare galena, gold and silver (Melchiorre and Enders, 2003). Fracture densities range from 0.1 to 1.0 cm^2, averaging 0.13/cm^2 in the Northwest Extension area (Preece, 1989).

Chalcopyrite is the only readily identifiable hypogene copper mineral. Molybdenite generally occurs as thin films on fractures devoid of other sulphides, but also occurs as thin streaks in small quartz veinlets. Zinc is present at only slightly lesser concentration than copper in the hypogene mineralisation, although it is normally entirely replaced in the supergene enrichment zone. The intense supergene clay alteration throughout the ore zone has obliterated the hypogene alteration, rendering it difficult to identify. (Melchiorre and Enders, 2003).

To the east of, and below the Morenci pit, drilling has encountered zones with a higher hypogene chalcopyrite:pyrite ratio which underlie the supergene sulphide enriched blanket at depth, and are surrounded laterally and above by a pyritic envelope. This chalcopyrite rich zone is interpreted to represent the centre of hypogene mineralisation. On the southern margin of the Laramide intrusive complex, mineralisation persists for almost 500 m into the Palaeozoic sediments where veins and replacement ore were developed. Oxidised veins and replacement mineralisation in this area were the principal source of ore in the early days of the district (Moolick and Durek, 1966).

The supergene enriched zone in the Morenci district covers an area approximately 7.5 km in a north-south direction and up to 4.5 km in width, divided into a number contiguous deposit area, including Morenci, Metcalf, Northwest Extension, Southside, Coronado and the Garfield Area in the north (Melchiorre and Enders, 2003).

The supergene profile at Morenci comprises a limonitic leached capping that overlies an enriched blanket containing high grade chalcocite ±covellite which has a three fold average enrichment of copper grades compared to the original hypogene mineralisation. The development of this profile began after deposition of the hypogene mineralisation at 56 to 55 Ma and continued through a number of progressive enrichment cycles as described below. Each involved uplift, erosion oxidation and leaching to further upgrade the succeeding supergene sulphide blanket. Where a subsequent supergene cycle encountered a blankets containing high grade chalcocite ±covellite mineralisation which had a low pyrite:chalcocite ratio (<2:1), the blanket was oxidised *in situ* to form an assemblage of brochantite, malachite, azurite, chrysocolla and other copper "oxides" as occurred in the Northwest Extension deposit (Melchiorre and Enders, 2003).

Lindgren (1905) described the supergene profile prior to significant exploitation. He reported that three district wide mineral zones could be recognised in the Morenci and Metcalf sections of the district. These were the i) surface, ii) chalcocite and iii) pyritic zones (now referred to as the leached capping, the zone of strong supergene enrichment and the zone of moderate to weak enrichment, respectively). The pyritic zone started at 60 to 180 m below the surface, and was not of economic interest in 1905 as it contained <1% Cu, although it carried chalcocite and other supergene copper minerals. The chalcocite zone, which was 30 to 120 m thick, yielded the richest ore, principally composed of chalcocite replacement of pyrite. In 1905, lean ore averaged between 2.0 and 2.5% Cu and regular ore was >2.5% Cu. Moolick and Durek (1966) noted that the supergene chalcocite ore zone with >1% Cu varied from 15 to 300 m in thickness. Lindgren (1905) reported that in places the chalcocite ore was almost at surface, while elsewhere hills of the oxidised surface zone (leached capping) rose to 60 to 90 m above the chalcocite blanket. This indicates that at some stage erosion has outpaced enrichment.

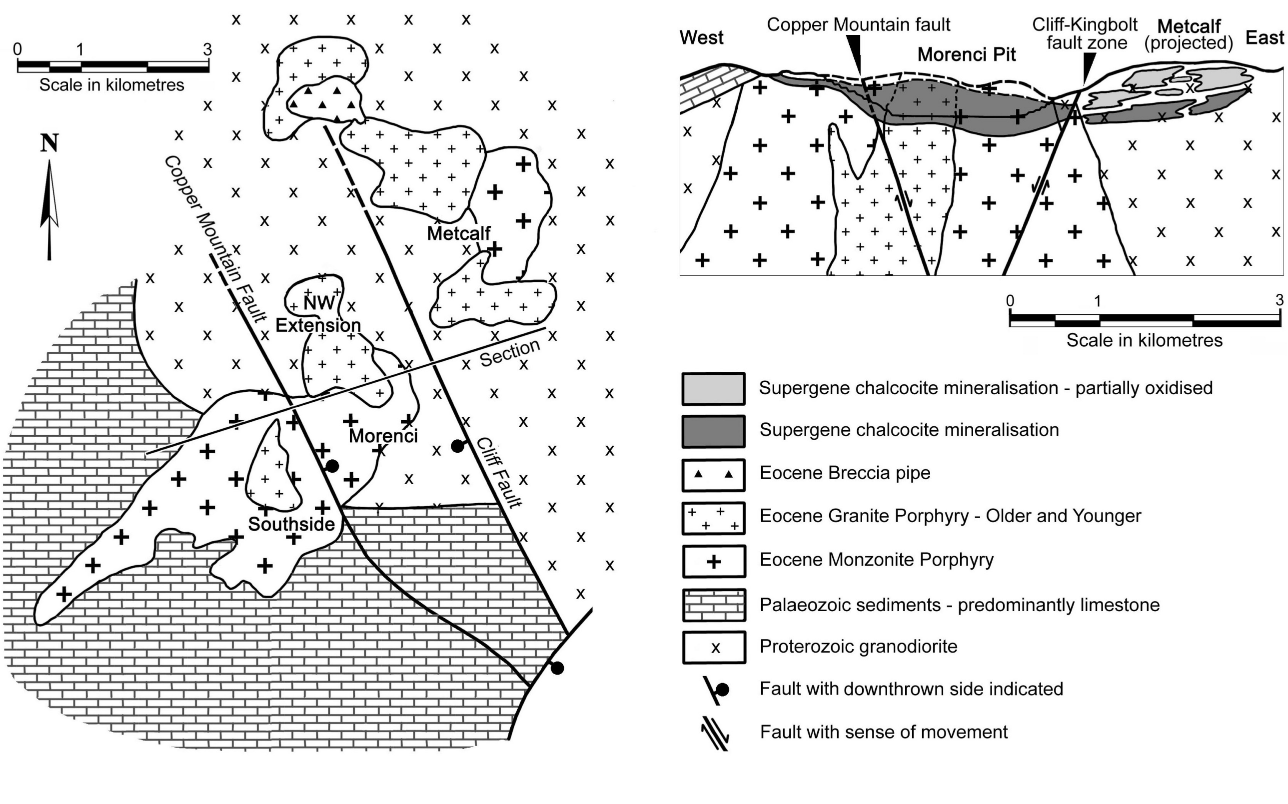


Figure 14: ***Geological sketch map and simplified cross section of the Morenci district, Arizona.*** The main chalcocite blanket in the Morenci district (known as the 'Clay Orebody') was located in a graben between two NNW trending normal faults, the Copper Mountain and Cliff faults. The graben is embedded in a larger horst, the southeast bounding fault of which is located on the bottom left of the plan. The district is surrounded on the margins of the plan area by Mid-Tertiary lavas and volcanic rocks, and Pliocene gravels (not shown). The cross section has a vertical exaggeration of 2 x the horizontal scale and is modified after Langton (1971). The 'Clay Orebody' enrichment blanket between the Copper Mountain and Cliff faults is more mature than the discontinuous mineralisation to the east of the Cliff fault, which was uplifted and partially oxidised, resulting in a new blanket being deposited at a lower level. During this same period, enrichment continued in the graben to produce a mature, higher grade chalcocite blanket.

The surface zone, as documented by Lindgren (1905), contained both gossans and deposits of chrysocolla, azurite, brochantite and malachite. Brochantite was formed from oxidation of chalcocite while malachite replaced brochantite (Lindgren, 1915). The best example of this is the 205 Mt @ 0.43% Cu Northwest Extension deposit to the north of the main Morenci pit, as described by Melchiorre and Enders, (2003). The Northwest Extension comprises an oxide zone (averaging 0.43% Cu) that is 250 m thick, bounded both above and below by low grade (0.08% Cu) leached capping. The lower zone of leached capping separates the oxide ore from a relatively thin, 14 to 45 m thick, high grade (0.68% Cu) enriched sulphide blanket and underlying hypogene (0.20% Cu) sulphide mineralisation (Melchiorre and Enders, 2003). Consequently, at some stage the current leached capping zone must have contained chalcocite, the product of an earlier phase of supergene enrichment, providing evidence of multiple stages of supergene activity.

The chalcocite ore within the main Morenci pit dips to the east at approximately 10° towards the composite NNW trending Cliff-Kingbolt Fault zone (Fig. 14) which corresponds to the eastern boundary of the main supergene ore. Movement on the Kingbolt Fault is mostly Laramide, although the latest movement on the Cliff Fault is no older than Miocene. A second major NNW trending structure, the Copper Mountain Fault, cuts across the Morenci pit and contains crushed chalcocite and chalcocite coated pyrite fragments within the fault zone. To the east of the Copper Mountain Fault the preserved leached capping is thin (averaging 15 m), but the enrichment blanket is thick (averaging 250 m). West of this same fault, the leached capping is approximately 250 m thick and the supergene sulphide zone if only 15 m thick. This difference is interpreted to indicate "stair-step" enrichment, where an already existing sulphide enrichment blanket in the western block was uplifted, leached during a subsequent episode of supergene activity with the copper migrating laterally into the eastern block. This is further evidence of multiple stages of supergene activity.

The Metcalf area to the northeast of Morenci, is characterised by a significant overlap between leached and enriched material and less thorough leaching than at Morenci, with many pockets of partially leached hypogene sulphides. Metcalf had lower grade hypogene mineralisation, but a higher pyrite content (3 to 5%). The host rocks typically contained more abundant biotite and were more reactive to supergene solutions than those at Morenci. Covellite, indicative of immature enrichment is also more abundant at Metcalf. Langton (1973) concluded that the difference lay in the overlapping of two stages of enrichment at Morenci to produce a higher grade and more mature blanket, while at Metcalf the two stages were separated, less mature, but developed over a thicker profile. Langton (1973) believed that the Metcalf deposits were upthrown by more than 350 m across the Cliff Fault during the Basin and Range Event, stranding the mineralisation above the water table, halting their enrichment, but subjecting them to further oxidation and the development of a separate, lower zone of enrichment. Alunite dates, discussed below support this conclusion. Moolick and Durek (1966) described oxide ore in contact with overlying basalts which are presumed to have been Miocene in age, although this exposure has since been removed by mining and the age of the basalt was not determined or recorded. Based on this observation and other evidence, Langton (1973) inferred there had been two episodes of supergene activity, one pre-volcanic, the other post-volcanic.

Two alunite samples were collected to the north of the Morenci pit. Sample UAKA 92-05 was from the hematite capping above the Morenci chalcocite blanket in the Northwest Extension area and comprised a pale green alunite taken from thin 3-4 mm, monomineralic veinlets cutting oxidised hypogene veinlets, hosted by the Laramide Older Granite Porphyry, in a road cut on Hennesey Hill. It came from about 2 m below the modern surface and yielded an age of 7.19 ±0.27 Ma. The second sample, UAKA 92-21 was from a mining bench in the Metcalf deposit, east of the Cliff Fault, 2.5 km east of Hennesey Hill and was within 25 m of the modern surface. This sample gave an age of 9.88 ±0.26 Ma. These results support the conclusion of Langton (1973) that supergene leaching and enrichment persisted longer at Morenci than at Metcalf.

Melchiorre and Enders, (2003) state that, based on work reported in Enders (2000) and others quoted therein, the first stage of supergene enrichment commenced after the emplacement of hypogene mineralisation in the Early-Eocene (56 to 55 Ma) and ended with the deposition of Mid-Tertiary volcanic cover during the Oligocene. Supergene activity resumed after 20 Ma and peaked when 'basin and range' uplift re-exposed the deposit. K/Ar dating (samples UAKA 92-05 and UAKA 92-21 described above) provides evidence of Late Miocene oxidation and supergene enrichment. The chalcocite deposits mined at Morenci probably formed during this period. The age of formation of the Palaeo-enrichment blanket which was weathered to produce the modern leached capping is inferred to have been pre-Oligocene.

Tyrone, New Mexico

Tyrone is a supergene sulphide enrichment blanket deposit developed over a low grade hypogene porphyry copper system, which has been preserved in a graben. Copper mineralisation is associated with slightly younger porphyritic phases of the 56.2 Ma Tyrone Stock. The hypogene mineralisation and alteration have been dated as Early-Eocene (56 to 53 Ma). Drilling shows that the Tyrone Stock actually comprises a series of porphyry dykes and laccolith like apophyses which intrude Proterozoic granites and to a lesser extent Cretaceous andesitic rocks that are found along the northeastern margin of the deposit. The deposit is represented at surface by heavily iron stained leached capping outcrops, although the northern section is covered by Miocene sediments and Pliocene alluvium. Palaeozoic rocks are absent from the district (duHamel *et al.,* 1995).

The Proterozoic is represented by: i) the *Burri Mountain Granodiorite,* an older, coarse grained granitoid with 10 to 20% books of biotite or chlorite; ii) the *Jack's Peak Quartz Monzonite,* a younger, medium grained, locally foliated quartz monzonite intrusive; and iii) *diabase* (dolerite) occurring as dismembered dykes striking east-west and cutting both granitoids; these dykes are almost always biotitised and are excellent hosts to hypogene sulphide mineralisation. The contacts between the two granitoid types are commonly the locus of Laramide intrusion. No Palaeozoic rocks are known in the district and the Proterozoic is directly overlain by a sequence of Cretaceous rocks commencing with a thin arkose, followed by several hundred metres of andesitic porphyry, agglomerate and andesite or dacite porphyry breccia which has been altered, both in the vicinity of the ore deposit and regionally (duHamel *et al.,* 1995).

The Proterozoic and Cretaceous rocks have been intruded by the 6x10 km Early-Eocene, Laramide Tyrone Stock (comprising a series of porphyry dykes and laccolith like apophyses, as described above) of overall quartz monzonite composition. The northeastern corner of this stock grades into porphyritic rocks which are responsible for the Tyrone hypogene mineralisation (Fig. 15). These porphyritic rocks are in turn composed of four stages as follows: i) *Stage 1 Porphyries,* which are porphyritic diorite and biotite-diorite porphyry with plagioclase and biotite phenocrysts in an aphanitic granophyric groundmass. These porphyries host well developed stockworks with a vein density of 10% by volume, accompanied by strong hydrothermal alteration, and fractured by the introduction of the Stage 2 Porphyries. ii) *Stage 2 Quartz-bearing Porphyries,* with intermediate granodiorite and tonalite compositions, sparse megacrysts of K feldspar, and quartz and biotite phenocrysts. At shallow levels they grade into a dacitic phase. These porphyries occur as north and northeast striking dykes traversing the orebody, cutting the Stage 1 Porphyries. They contain more disseminated sulphides than Stage 1, but have a lesser density of stockwork veining, rarely exceeding 5% by volume. They are considered to be the progenitor of hypogene mineralisation at Tyrone. iii) *Stage 3 Intrusive Breccia,* which are typically 60 to 120 m diameter elliptical masses composed of 20 to 60% rounded to subangular clasts of Proterozoic, Cretaceous and pre-Stage 3 Laramide lithologies, all set in a sulphide (chalcopyrite, sphalerite and pyrite) bearing rock flour matrix. They are cut by, but are closely associated with, Stage 2 dykes. Together the dykes and intrusive breccias form intrusive complexes that are centres of hydrothermal mineralisation. iv) *Stage 4 Laramide Rocks,* which include a 450 m diameter oval shaped tonalite porphyry plug and a series of dacite porphyry dykes, similar to those of Stage 2. None contain significant stockwork veining and generally have <0.5% disseminated sulphide, although they carry the strongest molybdenum mineralisation is the mine, averaging 0.08% MoS_2 (duHamel *et al.,* 1995).

Within the district, but not at the mine, all of the preceding rocks are unconformably overlain by 350 m of Oligocene volcanic rocks dated at between 32 and 27 Ma. Three unconformities, one of which is angular, have been recognised within this pile. These volcanics are conformably overlain by the Miocene Mangas Conglomerate which has been deformed by the Basin and Range tectonism and carries widespread, but low grade (>0.2% Cu) exotic copper mineralisation and scattered higher grade (>1% Cu) accumulations of up to 0.1 Mt. These are in turn overlain by scattered Pleistocene and Holocene alluvium (duHamel *et al.,* 1995).

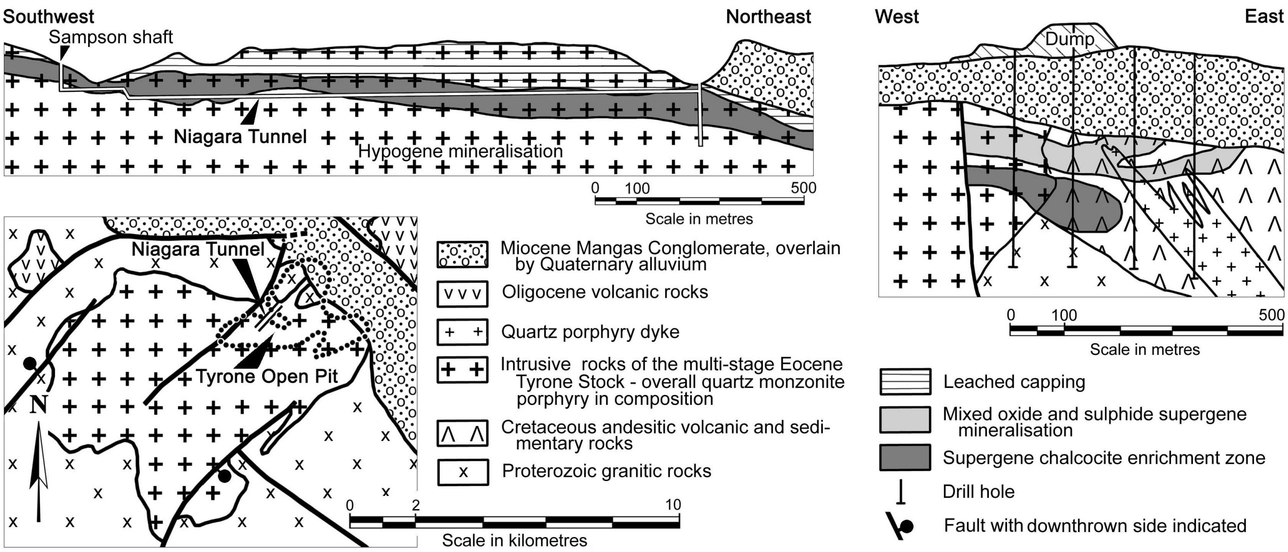


Figure 15: ***Geological plan and cross sections of the Tyrone supergene copper ore deposit, New Mexico.*** The geological plan (*lower left*) of the Tyrone district is after duHamel, *et al.,* (1995) and references cited therein. It shows the Tyrone Pit in the northeastern section of the Early Eocene, multi-phase, Tyrone Stock. The section above, (*top left*) is redrawn from an original mine pencil sketch dated 1916, and shows the distribution of ore prior to large-scale mining. The Mangas Conglomerate on that section has since been removed and does not appear in that location on the geological map which was published later in the century. Note the location of the Niagara Tunnel on both the section and on the geological plan. The outcrop of chalcocite near the Sampson Shaft illustrates how Holocene erosion outpaced chemical weathering and cut down into the chalcocite deposits. The section on the *top right* is located on the margins and beyond the northeastern lobe of the Tyrone Pit. Drilling showed the jarositic leached capping below the Mangas Conglomerate contained relatively abundant cuprite, native copper and residual chalcocite. A second horizon of chalcocite mineralisation was discovered beneath the partially destroyed upper horizon. The upper horizon was shown to be truncated by the erosion surface at the base of the Mangas Conglomerate. Note also that the faults appear to cut the chalcocite blanket but not the conglomerate, although alternatively, they could possibly pinch out before reaching the fault.

Hypogene mineralisation is hosted by Laramide intrusive rocks and the underlying Proterozoic granite. It is mostly associated with Stage 2 quartz porphyry intrusive centres which break through Stage 1 porphyries to form salients into the enclosing Proterozoic and Cretaceous wall rocks. Primary copper and molybdenum mineralisation occurs as chalcopyrite and molybdenite bearing stockwork vein systems at depths of 300 to 450 m below the base of the open pit, within potassic altered hosts immediately below the transition to the overlying phyllic alteration zone. The chalcopyrite and molybdenite stockwork veining carries grades of 0.2% Cu and 0.02% MoS_2, while 0.4% Cu as chalcopyrite accompanying magnetite persist to depths of 1000 m. However, while this mineralisation is found at depth, evidence of chalcopyrite in supergene enriched stockwork ores is rare near surface and within the chalcocite blanket ores. The dominant hypogene sulphide in the open pit zone is pyrite, which contains small inclusions of quartz and chalcopyrite. The hypogene mineralisation in the open pit averaged less than 6% sulphide by weight. Unless all primary chalcopyrite was been completely replaced during supergene enrichment, the copper of the chalcocite blanket would have been derived from the low grade copper values associated with the pyrite mineralisation (duHamel *et al.,* 1995; Kolessar 1966).

The supergene orebody at Tyrone is roughly triangular in shape with sides each of approximately 3.5 km. Although the upper surface is very irregular, the supergene sulphide enrichment blanket is generally tabular and slopes at 8°NW. It varies from a few metres to more than 100 m in thickness and is overlain by a comparable remnant thickness of leached capping (60 to 150 m thick), which has been locally dissected to the sulphide zone along one deep drainage channel (Fig. 15). More supergene ore is hosted by Proterozoic granite intruded by Laramide porphyry dykes, than in the actual Laramide intrusives. However the richest ore, which averages over 1% Cu, is hosted by the Laramide intrusive breccia. A breccia body exposed in the North Pit, has complete replacement of pyrite at 180 m below the pre-mine surface, and 15 to 30% replacement 60 m lower (duHamel *et al.,* 1995; Kolessar 1966).

Sooty chalcocite, with lesser covellite, is the predominant supergene ore minerals. Chalcocite replaces chalocopyrite, sphalerite and pyrite, thereby filling interstitial spaces in the breccia. In the other lithologies, chalcocite has replaced sulphides in veins, and as dissemination, but has also been deposited in open spaces, while in some instances only disseminated chalcocite has been found, with the original fracture controlled hypogene sulphide having been completely leached/replaced. There are at least 20 areas in the mine where partially mined out high grade zones from the early 20th century underground operation average 2 to 3% Cu. In areas where older supergene enrichment stages have been re-weathered, the most abundant oxide minerals are chrysocolla, black copper silicates and black copper oxides such as melaconite and 'copper-wad', mixed with limonites (duHamel *et al.,* 1995; Kolessar 1966).

The supergene orebody in the open pit is overlain by a jarosite-hematite leached capping which can be followed to the northeast, where it passes under the Miocene Mangas Conglomerate. Below the conglomerate, two layers of supergene chalcocite can be resolved (Fig. 15). The upper blanket consists of abundant sooty chalcocite, cuprite, native copper and minor steel-glance chalcocite. The lower supergene sulphide enrichment layer is dominantly steel-glance chalcocite with only minor sooty chalcocite. The gap between the two, occupied by leached capping, is evidence that each represent a distinct temporal stage of weathering and enrichment. Both enrichment blankets have been offset the same amount across normal faults which are mineralised by small, but very high grade deposits of sooty and steel-glance chalcocite. This fault controlled set of chalcocite veins which cut both blankets represents a third stage of supergene enrichment.

Oxidation and supergene alteration was apparently initiated during the Eocene. It is likely that the Oligocene volcanic units immediately to the east of the mine interrupted weathering and supergene activity, although the evidence is only circumstantial. However it is apparent that a mature supergene profile existed by the Middle Miocene. The development of this profile included the uplift and oxidation of the upper enrichment blanket leaving a layer of hematite rich leached capping over much of the deposit. The upper, partially oxidised chalcocite blanket was preserved below the remaining Mangas Conglomerate where it was protected from compete destruction by post-Miocene oxidation. Subsequent erosion of the conglomerate from over the majority of the deposit started a new cycle that totally leached the exposed upper blanket. This cycle was interrupted by the Basin and Range Event that again changed the hydrologic conditions in the district. The latest episode of supergene activity has involved mineralisation of 'basin and range' fault structures and the deposition of exotic copper mineralisation, some of which is visible in the pit walls. Where sufficient pyrite remained, further copper was leached from the Miocene and Eocene chalcocite deposits. Otherwise chrysocolla and malachite oxide-copper mineralisation was formed *in situ* during the Late-Miocene to Pliocene (duHamel *et al.,* 1995).

Four supergene samples were taken from Tyrone (see Table 2). The oldest, UAKA 92-22, which was dated at 39.5 ±1.7 Ma, was a submicron illite hosted by an intrusive breccia. It was collected from the 5450 bench on the northern wall of the North Pit. This determination is subject to the uncertainty discussed in the 'Introduction' section, but is interpreted to represent the first stage of supergene enrichment after erosion removed the andesite volcanic complex edifice above the porphyry deposit and exposed the hypogene mineralisation, prior to the onset of Oligocene volcanism. Two Middle Miocene dates record the second episode of supergene activity involving the destruction of the upper chalcocite blanket and the formation of the lower supergene sulphide enrichment horizon, prior to deposition of the Mangas Conglomerate. The older of these, 19.2 ±0.4 Ma, was from sample UAKA 91-77, an alunite from a 20 mm thick, monomineralic veinlet in the pre- 'Basin and Range' Crusher Fault. The second Middle Miocene date of 16.2 ±0.4 Ma, from sample UAKA 92-56 was a hand picked light beige alunite from a thin (1 to 2 mm) veinlet cutting Proterozoic quartz monzonite on the 5750 level of the open pit. The Late-Miocene age of 8.46 ±0.4 Ma from sample UAKA 92-55 dated a pale green alunite which also occurred in thin veinlets cutting Proterozoic quartz monzonite on the 5750 level, approximately 60 m northeast of sample UAKA 92.56. This latter date is more difficult to interpret, as it is likely that the 'basin and range' faulting in the district preceded this, so it may record oxidation related to mineralisation within 'basin and range' structures.

Santa Rita, New Mexico

The Santa Rita deposit (exploited by the Chino open pit mine) lies on the northern margin of the Basin and Range province in southwestern New Mexico. It also lies near the northern margin of the Palaeozoic depositional basin. Only a few questionable outcrops of Proterozoic basement have been recognised. The basal Palaeozoic sequence comprises Cambrian sandstone, Ordovician and Silurian dolomites and dolomitic limestone, and Devonian shales. In the Santa Rita area the Palaeozoic is principally represented by Carboniferous limestones, cherty limestones and limy shales that constitute the Lake Valley Limestone, and the unconformably overlying Oswaldo and Syrena Formations. These units are followed by the Permian Abo Formation red shale, limestone and limestone conglomerate. The Palaeozoic sediments are in turn unconformably overlain by the 30 m thick Late Cretaceous Beartooth Quartzite, which in addition to quartzite includes limy sandstone and shaly sandstone. This unit is succeeded by the 300 m thick Late Cretaceous Colorado Formation comprising a lower black shale unit and upper sandstones. These Palaeozoic and Mesozoic sediments together constitute a pile of around 1200 m in thickness (Rose and Baltosser 1966).

The first magmatism in the district commenced during the Late Cretaceous to early Tertiary with the intrusion of a series of sills and laccoliths of diorite, porphyritic quartz diorite and related rocks. The quartz diorites were emplaced as multiple intrusions of two ages, an Early and a Late Quartz Diorite with different textures and phenocryst compositions. These intrusions were followed by the deposition at surface of 100 m or more of andesite breccia, tuff and lesser intercalated sandstone and shale. The quartz diorites were succeeded by the next major magmatic event, represented by the Late Paleocene 63 Ma granodiorite porphyry of both the Santa Rita Stock, and the Fierro-Hannover Stock 5 km to the north. These two stocks are related to the formation of porphyry style mineralisation. They have a variable composition, but in general contain phenocrysts of plagioclase (andesine), hornblende, thick biotite books and sparse quartz in a groundmass of anhedral quartz, orthoclase, minor biotite and accessories. Two thick granodiorite porphyry dykes with similar compositions extend northward from the Santa Rita stock. These and other similar dykes in the vicinity may be apophyses of the stock, although some also cut both stocks and may post date the mineralisation.

North-south trending dykes of quartz monzonite porphyry, common in the district, cut the Santa Rita Stock. These latter dykes are distinguished by large phenocrysts of orthoclase and a greater abundance of quartz. While some copper post dated these dykes, the bulk of the copper and zinc mineralisation preceded their intrusion. A further quartz monzonite porphyry dyke cuts across the Santa Rita Stock in a northwest direction. Fragments of this dyke are found in a steep sided, localised basin of conglomerate and sandstone, the Wimsattville Formation, which is interpreted to represent a crater or caldera. These sediments are in turn cut by dykes of latite and quartz latite which are common throughout the district, including and east-west trending set which cut the Santa Rita Stock, but appear to be older than the Miocene volcanics (Rose and Baltosser 1966).

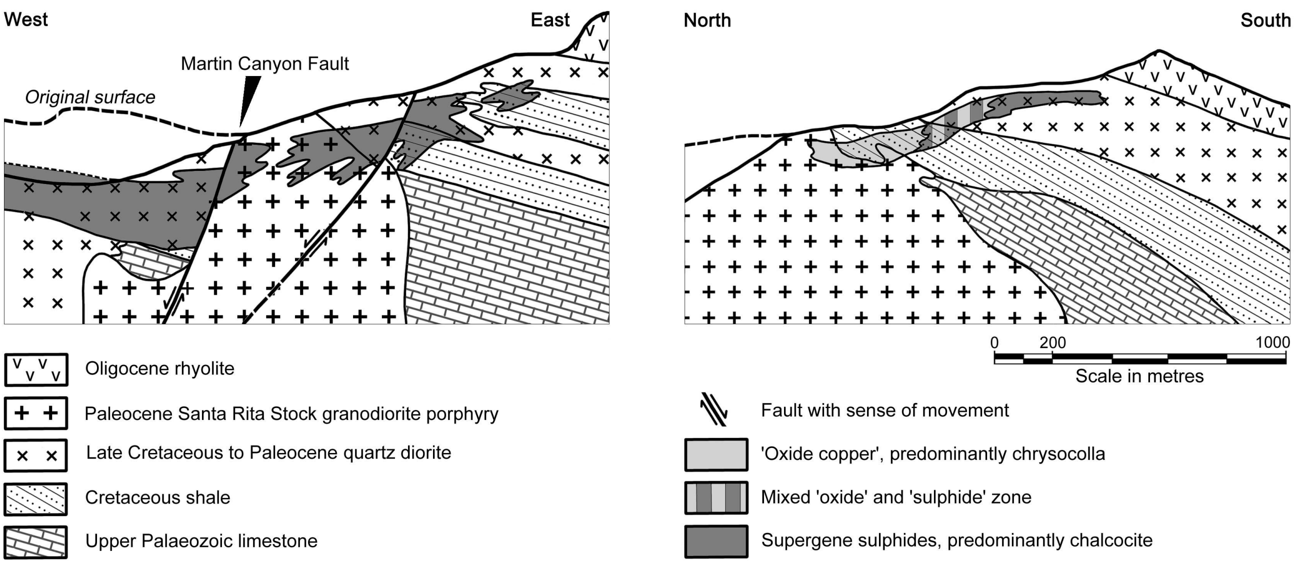


Figure 16: ***Geological cross sections across the Santa Rita supergene copper ore deposit, New Mexico.*** The east-west section (*left*) illustrates how chalcocite mineralisation is offset as two "stair steps" by post-volcanic faulting. Enrichment is best developed around the periphery of the Santa Rita Stock. The centre of the intrusion is devoid of copper in many areas. The north-south section (*right*) through the supergene blanket, in the southeast section of the deposit, shows a lateral zoning within the blanket with respect to the outcrop of the capping Oligocene rhyolite, reflecting the progressive unroofing and oxidation of the buried supergene mineralisation.

The sedimentary, volcaniclastic and intrusive rocks detailed above were subjected to considerable erosion prior to the deposition of Oligocene volcanic rocks of the 36.9 Ma Sugarlump Tuff, the 33.4 Ma Kneeling Nun Rhyolite and late Oligocene basaltic andesites to the south of the Santa Rita Stock. Erosion and deposition of Miocene to Pliocene consolidated sand, gravel silt and clay occurred during the Basin and Range Event, accompanied by minor amounts of volcanic rocks. These were overlain by recent alluvium. The sequence within the district has been subject to complex faulting, while the generally shallow dipping Palaeozoic to Mesozoic sedimentary sequence has been structurally disrupted by the intrusion of the Laramide stocks (Rose and Baltosser 1966).

The 4 km diameter Santa Rita Stock, composed mostly of granodiorite porphyry, intrudes most units of the Carboniferous to Cretaceous sequence described above. Two styles of ore have been mined historically at Santa Rita, namely: i) *supergene enriched copper ore* developed over hypogene porphyry copper mineralisation, comprising mainly chalcocite, and hosted by the intrusions and by wall rocks of Upper Palaeozoic sandstones and shales and ii) *skarn ore* developed within Upper Palaeozoic carbonates adjacent to the Santa Rita and Fierro-Hannover Stocks, composed mainly of chalcopyrite, accompanied by major amounts of magnetite, pyrite, quartz and garnet, as well as epidote, tremolite-actinolite, and by chlorite in more impure limestone hosts (Rose and Baltosser 1966).

Hypogene porphyry style copper mineralisation at Santa Rita comprises disseminated and veinlet chalcopyrite and pyrite with only minor bornite and small amounts of molybdenite, pyrrhotite and marcasite. Chalcopyrite tends to be more prevalent as disseminations, while pyrite, which is ubiquitous and much more abundant than chalcopyrite, is more obvious in the veinlets. The hypogene grade, in general, ranges from 0.1 to 0.3% Cu, with around 4% pyrite within the porphyry host below the supergene ore. The principal alteration assemblage within the Santa Rita Stock comprises orthoclase, biotite, quartz with clay (probably supergene) and some sericite. Orthoclase also occurs within veinlets with the quartz and sulphides. On the margins of the stock and in siliciclastic sediments and quartz diorite of the wall rocks, the dominant alteration minerals are sericite and quartz, with copper grades similar to those in the granodiorite porphyry, and sulphides concentrated in veins. Within the carbonate hosts, ore grade hypogene mineralisation has been developed with little or no supergene enrichment. Chalcopyrite typically occurs as veinlets and disseminations within the skarn mineralogy. On a broader scale there is a zonation outwards from the centre of the Santa Rita Stock of copper to copper-zinc to lead-zinc (Rose and Baltosser 1966).

Prior to mining, supergene mineralisation was present as three northwest trending zones of relatively thick, high grade chalcocite ore. In general, these three zones correspond to mineralisation developed along the northeast and southwest margins of the Santa Rita Stock, straddling the contacts and hosted by both granodiorite porphyry and siliciclastic rocks, while the third occupied a broader central zone over the core of the main stock. The dominant sulphide is chalcocite, with minor covellite, while where oxidised, native copper, chrysocolla, cuprite, malachite and azurite are important minerals. Both sooty and steel-glance chalcocite are present, either as veins or discrete grains composed only of chalcocite, or as coatings on pyrite, and at greater depths as partial replacement of chalcopyrite. The preserved goethite-hematite-jarosite leached capping (which was rose coloured in outcrop) varies from a few to more than 100 m in thickness, while the underlying supergene enriched sulphide blanket ranges from a few to over 200 m, although appreciable amounts of chalcocite are present partially replacing hypogene sulphides at depths of more than 250 m (Rose and Baltosser 1966).

Three stages of supergene enrichment have been distinguished at Santa Rita. Evidence for the first stage is from both chalcocite mineralisation buried below the Oligocene (33.4 Ma) Kneeling Nun Rhyolite and clasts of chalcocite ore and leached capping in the basal conglomerate of that unit, immediately to the southeast of the Santa Rita Stock. The second stage, believed to be Oligocene to Miocene in age, is inferred from detailed geological cross sections, prepared from drilling and mining information (Fig. 16). These sections reveal that chalcocite mineralisation thickened abruptly northwards, away from the Oligocene volcanic overburden, but is offset by around 150 m across the late Miocene or Pliocene Martin Canyon Fault. This fault is believed to be a ‘basin and range’ structure, active at around 12 Ma. An immature weathering profile is developed in the footwall of this same fault, in which isolated bodies of un-oxidised (chalcocite), or partially oxidised (chrysocolla and malachite mixed with chalcocite) primary and secondary sulphides of the main supergene chalcocite blanket are embedded in ‘oxide copper’ mineralisation and leached capping, above the main chalcocite blanket. This observation is taken to imply that post-Miocene supergene processes were active, but relatively inefficient after the Basin and Range Event at Chino, defining a third stage of supergene activity. Supergene enrichment had concluded by the Quaternary when the modern surface was incised through the enrichment profile and the supergene enrichment blanket.

Further evidence for post-Miocene supergene processes is illustrated by the north-south cross section from the southeastern part of the deposit shown on Fig. 16. In this area there is a lateral zonation within the supergene blanket with respect the outcrop of the overlying Oligocene rhyolite. This zonation reflects the progressive unroofing and oxidation of the pre-Oligocene supergene blanket. The supergene mineralisation is developed in a relatively homogenous, highly altered (quartz, sericite, K feldspar and pyrite) host of shale and diorite, and hence the results of post-volcanic weathering can be isolated. Chrysocolla predominates furthest to the north, along the southeastern margin of the stock. Further south, towards the more recently exposed parts of the supergene blanket, there is a transition through a mixed oxide-sulphide zone, to un-oxidised chalcocite. The oxidation is the result of post-volcanic weathering of a mature enrichment blanket. The leached capping thickens to the west, in the downthrown block (as shown on the east-west section on Fig. 16) and the chalcocite ore was largely not influenced by oxidation.

Two supergene alunite K/Ar dates have been determined from the Chino mine area. The younger of these is Late Oligocene (25.6 ±0.7 Ma), returned from sample X-10606, which was taken from a monomineralic veinlet preserved within hematitic leached capping less than 30 m below the modern surface. The sample is considered supergene on the basis of field occurrence alone, and is interpreted to represent the earliest activity in the second stage of supergene enrichment, following removal of Oligocene volcanic cover. The older date of early Oligocene 34.3 ±0.9 Ma from sample UAKA 93-11 is more problematic. There is strong evidence that during the Early-Oligocene, the Santa Rita District was covered by in excess of 100 m of volcanic cover (Hernon and Jones, 1968). This sample was taken from 210 m below the modern (pre-mine) surface. It is isotopically heavy (1.7‰ $\delta^{34}S$) compared to the typical hypogene sulphides in the Chino mine (-2.1‰ $\delta^{34}S$; Field, 1966), although the difference is not extreme. The contribution of isotopically heavy sulphur from hypogene sulphates cannot currently be quantified, although it is reasonable to conclude that some is taken up by supergene sulphates during weathering. The older alunite may be the product of subvolcanic diagenesis or hydrothermal activity involving meteoric waters trapped by the virtually instantaneous deposition of volcanic tuffs, and heated by prolonged volcanic activity. Alternatively it could be a hybrid date resulting from growth of Miocene alunite on Eocene grains or partial re-equilibration of very fine grains during different periods of supergene activity.

Discussion

Regional Correlations

Episodes of supergene sulphide enrichment must correlate with an erosional surface, as they are essentially the result of a form of chemical weathering (Segerstrom, 1963; Clark *et al.,* 1967; Sillitoe *et al.,* 1968; Mortimer 1973, 1977). This erosional surface can be either the modern landscape or an ancient surface. The modern (pre-mining) landscape correlated with the top of supergene mineralisation at Silver Bell, Pinto Valley (Castle Dome) and Bisbee. K/Ar dating corroborates this at Silver Bell and at Bisbee, but not at Pinto Valley. A somewhat different correlation between supergene mineralisation and the modern landscape exists at Ajo where the base of sulphide oxidation in the untilted supergene ores was the (pre-mine) modern water table. Fig. 17 shows the deposits which have either stratigraphic, geomorphic or isotopic (K/Ar) evidence of Late Miocene or Pliocene supergene alteration.

There is no evidence at Lakeshore, Sacaton and Santa Cruz of significant supergene activity since the Basin and Range Event began. All three of these deposits are located in the mature desert landscape which exists west of the Santa Cruz River (Fig. 17) where erosion now predominates over chemical weathering. Many physiographic features in this landscape apparently date back to at least the Middle Miocene (Damon *et al.,* 1974; Shafiqullah *et al.,* 1980). Ajo and Silver Bell, with similar modern climates, have clearly undergone significant supergene activity since the beginning of the Basin and Range Event.

The absence of supergene activity since the Late Miocene at Lakeshore, Sacaton and Santa Cruz is due to the lack of pyrite in the weathering zone, not the locally semi-arid climate. All three deposits are in the hangingwall of 'basin and range' faults, while Ajo and Silver Bell are in the footwall of similar structures.

Fig. 17 also shows those deposits with evidence of Late Oligocene to Middle Miocene supergene activity. This same period is the most favourable for supergene activity in the Andean Cordillera of northern Chile (Brimhall and Mote, 1997; Mote and Brimhall, 1997; Sillitoe and McKee, 1996). Clearly this was also an important period of enrichment in Arizona and New Mexico. However, unlike northern Chile, where extreme aridity ended significant supergene alteration at most major deposits at approximately 15 Ma (Brimhall and Mote, 1997; Alpers and Brimhall, 1988), sulphide enrichment and *in situ* oxidation of older supergene sulphide ores continued in southerwestern US during the late Miocene and well into Pliocene time.

There is a correlation between an Eocene to Early-Oligocene erosion surface and the top of the tilted chalcocite mineralisation at Ajo and San Manuel. Fig. 17 also shows deposits or districts with evidence of Eocene or Early-Oligocene supergene alteration. Livingston *et al.,* (1968) list many districts where supergene ores were buried and preserved by Mid-Tertiary volcanic rocks. These districts are not indicated on Fig. 17, which only shows the location of evidence considered in the investigation reported herein. Finally, a correlation exists between the top of sulphides (base of oxidation) in limestone replacement/skarn deposits at Bisbee and an Early-Cretaceous surface. This is the only known example of Early-Cretaceous supergene activity in the region.

Scarborough (1989) summarised the Cenozoic stratigraphy of southern Arizona and adjacent parts of New Mexico. The diagram on the left side of Fig. 18, redrawn from Scarborough (1989), provides a graphic illustration of the Cenozoic stratigraphy in southwestern U.S. as a base for discussing regional correlations of supergene activity. This diagram shows four tectono-stratigraphic units, bounded by time-transgressive regional unconformities, which, in general, young to the west. These four units are: i) the *Whitetail Assemblage* of continental sediments which were deposited during the Eocene Epeirogeny and have generally been tilted (Shafiqullah *et al.,* 1980). ii) *Volcanic units* deposited during the Mid-Tertiary Orogeny. iii) the *San Manuel Assemblage,* comprising continent sediments, which have often been tilted, and were deposited after Mid-Tertiary volcanism, but prior to 'basin and range' activity. iv) The *Gila Assemblage,* of continental sediments deposited in modern basins. None of these assemblages completely covered the region, and it is possible they may be an over-simplification of the actual sequence in some districts.

The plot on the right side of Fig. 18 shows the supergene K/Ar dates from this study plotted on the Scarborough diagram. The dates from Sacaton and Tyrone fall, more of less, on the erosion surface between the Laramide and pre-Laramide bedrock, and the Whitetail assemblage. The first cycle of enrichment at Ajo and the chalcocite blanket at Kalamazoo correlate with this same erosion surface as well, based on stratigraphic evidence. The apparent poor correlation at Sacaton is, in large part, due to the lack of datable Oligocene units in the vicinity of the deposit.

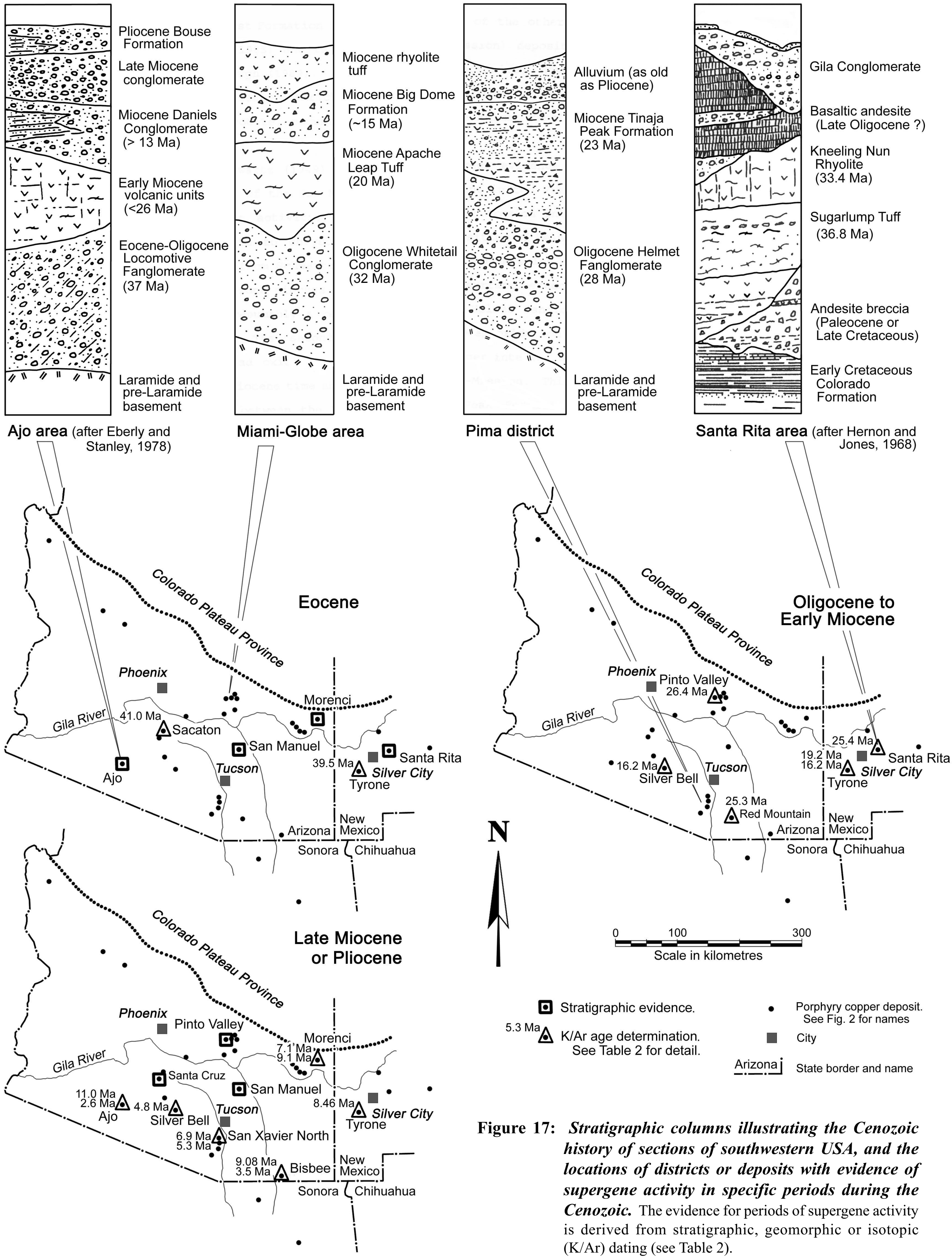


Figure 17: ***Stratigraphic columns illustrating the Cenozoic history of sections of southwestern USA, and the locations of districts or deposits with evidence of supergene activity in specific periods during the Cenozoic.*** The evidence for periods of supergene activity is derived from stratigraphic, geomorphic or isotopic (K/Ar) dating (see Table 2).

The dates from Pinto Valley and Red Mountain correlate closely with the erosion surface between the Whitetail Assemblage and the Mid-Tertiary volcanics. This erosional surface, where preserved, is often an angular unconformity due to the widespread deformation by the Mid-Tertiary Orogeny of the local basins formed during the Eocene Epeirogeny. Enrichment at Lakeshore, Santa Cruz, Inspiration, Santa Rita (Chino) and probably Morenci occurred in Whitetail time, where deposition was only restricted to local basins during the Eocene Epeirogeny, while most of the region was exposed and being weathered.

Dates from Santa Rita (Chino),Tyrone and Silver Bell all fall reasonably close to the regional unconformity at the top of the Mid-Tertiary volcanic assemblage.

The K/Ar dates from the late Miocene and Pliocene do not plot close to the San Manuel Assemblage-Gila Assemblage unconformity, but are all younger. The Gila Assemblage correlates with the Basin and Range Event, when deposition was restricted to elongate basins separated by extensive exposed, ranges. Clearly, where sulphides, or other reactive supergene minerals were exposed to the atmosphere by 'basin and range' faulting, weathering continued and supergene alteration persisted well into Pliocene time.

Each tectonic pulse in the geologic evolution of the region has had an impact on hydrologic conditions, either because of uplift, or changing local base levels, which facilitated episodes of supergene activity at several porphyry copper deposits.

Supergene Alteration and Climate

Global climatic patterns have been suggested as controlling factors in supergene activity (Brimhall and Mote, 1997; Mote and Brimhall, 1997; Vasconcelos *et al.,* 1997) during Early-Oligocene to Middle Miocene time. The palaeoclimatic history of Arizona and New Mexico was reviewed by Nations *et al.,* (1985) on the basis of the fossil record. The Paleocene climate in the region was humid and warm-temperate to sub-tropical. Pollen records in Eocene sediments with a provenance in Arizona contain plant taxa living today in both cool temperate uplands and sub-tropical lowlands. A pattern of well drained uplands and poorly drained lowlands persisted into early Oligocene time.

Mid-Tertiary volcanism disturbed the existing pattern of microclimates and appears to have made the overall climate cooler, drier and more variable than in the Eocene (Scarborough, 1989; Nations *et al.,* 1985). Plant and animal fossils are relatively common in the Miocene-Pliocene of the region, and a wide variety of palaeobiological communities are preserved, indicative of palaeoclimates governed by palaeotopography. The region developed an interior drainage pattern during the Miocene, culminating in the deposition of large evaporate deposits (Shafiqullah *et al.,* 1980). Thus, the region was largely isolated from the hydrological repercussions of Late Miocene changes in sea level which affected supergene activity elsewhere (Brimhall and Mote, 1997). The palaeoclimatic history of southwestern U.S. is complex and a detailed analysis of the influence of microclimates on the supergene chronology of each deposit or district has not been undertaken.

The copper in Pleistocene and younger sediments in the region is predominantly detrital chrysocolla and tenorite (Huff 1970; Lovering *et al.,* 1950). This is taken as evidence that erosion dominated over chemical weathering during this period and consequently near surface conditions in southwestern U.S. did not favour significant supergene enrichment during the Holocene. Never the less, weathering of sulphides continues in the present climate, although the rate of oxidation appears to have slowed approximately 30 000 years before present (Lovering, 1949). Patterns of precipitation changed during the Pleistocene, to a more seasonal, monsoonal pattern of rainfall which promoted

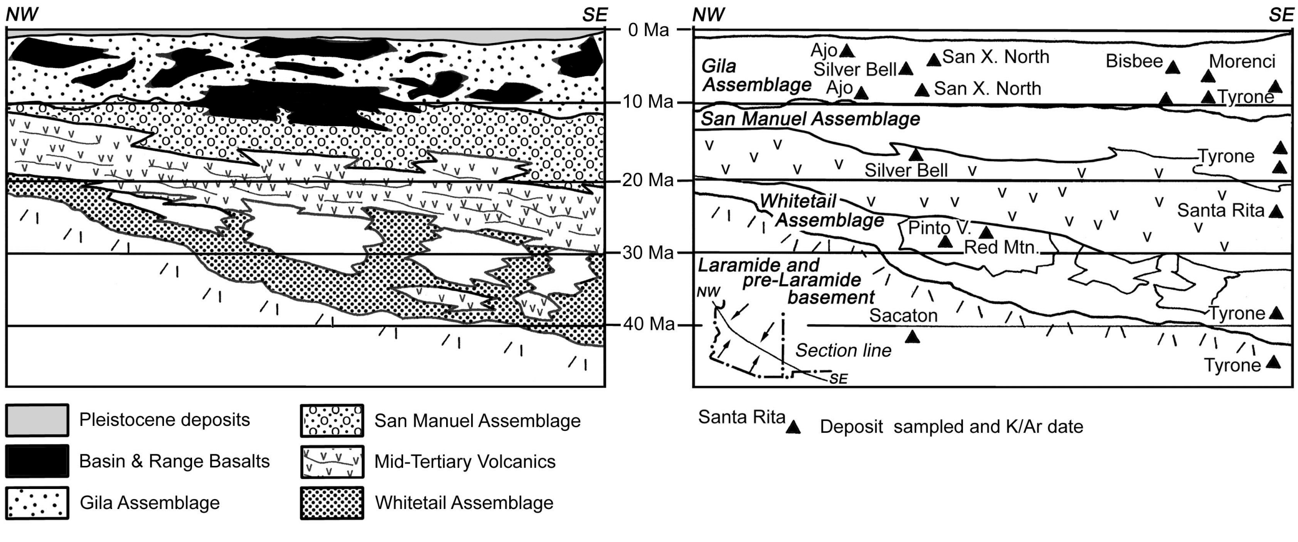


Figure 18: ***Diagrams comparing the K/Ar dates of supergene activity affecting porphyry copper deposits and Cenozoic erosion, sedimentation and volcanism in southern Arizona and adjacent New Mexico.*** Four time transgressive strato-tectonic assemblages have been interpreted and correlated across the region. These unconformity bounded assemblages are the result of the Eocene Epeirogeny (Whitetail Assemblage), Mid-Tertiary Orogeny (Mid-Tertiary volcanics), post volcanic extension and listric faulting (San Manuel Assemblage) and the Basin and Range Disturbance (Gila Asemblage). The diagram on the left is after Scarborough (1989). The diagram on the left shows the same four assemblages, with supergene K/Ar dates from the sampling program superimposed. See Fig. 17 for actual stratigraphic columns representing these assemblages across the region.

arroyo cutting (steep sided ephemeral watercourses in unconsolidated material) throughout the region (Nations *et al.,* 1985). Supergene sulphides, and in some cases primary sulphides, were exposed in canyons (gorges) where leached cappings had been rapidly eroded by intense monsoonal precipitation.

Conclusions

The porphyry copper deposits in Arizona and New Mexico have undergone supergene alteration for as long as sulphide minerals have been present in the zone of oxidation. Contemporaneous supergene activity during the: i) Eocene at Santa Rita, Tyrone, San Manuel (and Kalamazoo), Inspiration, Sacaton and Ajo; ii) Late Oligocene to Middle Miocene at Santa Rita, Tyrone, Red Mountain, Pinto Valley, Lakeshore and Silver Bell; and iii) Late Miocene to Pliocene at Tyrone, Morenci, Bisbee, San Manuel, Pinto Valley, San Xavier North, Silver Bell and Ajo, is the result of the common tectonic history they all share to varying degrees.

Most of the porphyry deposits in the region, most notably Ajo, San Manuel, Morenci, Tyrone, Bisbee, Santa Rita and Santa Cruz have undergone multiple episodes of supergene activity, separated by millions of years, and often by profound tectonic changes in local geology.

Evidence of separated episodes of supergene activity, in the form of stratigraphic relationships, or K/Ar dates, begins in the Early-Cretaceous at Bisbee and continues until the Pliocene at Bisbee, Ajo, Silver Bell and San Xavier North.

Copper enrichment occurred in both the warm sub-tropical climate of the Eocene and the semi-arid conditions of the Pliocene. The oxidation and supergene enrichment of porphyry copper deposits in Arizona and New Mexico has apparently continued through diverse climatic regimes, at least locally. That is, the enrichment is likely an edaphic rather than climatic phenomenon.

References

Alpers, C.N. and Brimhall, G.H., 1988 - Middle Miocene climatic change in the Atacama Desert, northern Chile: Evidence from supergene mineralization at La Escondida: *Geol. Soc. America* Bull., v. 100, pp. 1640-1656.

Anderson, J.A., 1982 - Characteristics of leached capping and techniques of appraisal: *in* Titley, S.R., (Ed.), 1982, Advances in Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 275-296.

Anderson, P.W., 1989 - Cyprus Miami Mine Geology: unpublished Mine Engineering and Geology Department, *Cyprus Miami Mining Corporation* Report, 5p.

Arehart, G.B., Kesler, S.E., O'Neil, JR. and Foland, K.A., 1992 - Evidence for the supergene origin of alunite in sediment-hosted micron gold deposits: *Economic Geology,* v. 87, pp. 263-270.

Ashley, R.P. and Silberman, M.L., 1976 - Direct dating of mineralization at Goldfield, Nevada, by potassium-argon and fission-track methods: *Economic Geology,* v. 71, pp. 904-924.

Atwood, W.W., 1916 - The physiographic conditions at Butte, Montana, and Bingham Canyon, Utah, when copper ores in these districts were enriched: *Economic Geology,* v. 11, pp. 697-740.

Barton, M.D., Staude, J.G., Zürcher, L. and Megaw, P.K.M., 1995 - Porphyry copper and other intrusion-related mineralization in Mexico: *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995, Porphyry Copper Deposits of the American Cordillera: *Arizona Geol. Soc.* Digest 20, pp. 487-524.

Bird, M.I., Chivas, A.R. and McDougall, I., 1990 - An isotopic study of surficial alunite in Australia, 2. Potassium-argon geochronology: *Chemical Geology* (Isotope Geosciences Section), v. 80, pp. 133-145.

Bladh, K.W., 1982 - The formation of goethite, jarosite, and alunite during the weathering of sulfide bearing felsic rocks: *Economic Geology,* v. 77, pp. 176-186.

Blanchard, R., 1968 - Interpretation of leached outcrops: *Nevada Bureau of Mines* Bulletin 66, 196p.

Bodnar, R.J. and Beane, R.E., 1980 - Temporal and spatial variations in hydrothermal fluid characteristics during vein filling in perore cover overlying deeply buried porphyry copper type mineralization at Red Mountain, Arizona: *Economic Geology,* v. 75, pp. 876-893.

Bonillas, Y.S., Tenney, J.B. and Feuchere, L., 1916 - Geology of the Warren Mining District*: AIME Transactions,* v. 55, pp. 284-355.

Brimhall, G.H. and Mote T.I., 1997 - Optimal secondary mineralization in the Andes: Vadose response to global Cenozoic cooling events, glaciation, eustacy and desiccation: *Geol. Soc. America* Abstracts with Program 1997, Salt Lake City, p. A-17

Bryant, D.G., 1968 - Intrusive breccias and associated ore of the Warren (Bisbee) Mining District, Arizona: *Economic Geology,* v. 63, pp. 1-12.

Bryant, D.G. and Metz, H.E., 1966 - Geology and ore deposits of the Warren Mining District: *in* Titley, S.R. and Hicks, C.L., (Eds.), Geology of the Porphyry Copper Deposits, Southwestern North America: *University of Arizona Press*, Tucson, pp. 189-203.

Christiansen, R.L. and Yeats, R.S., 1992 - Post-Laramide geology of the U.S. Cordilleran region; *in* Burchfiel, B.C., Lipman, P.W. and Zoback, M.L., (Eds.) 1992, The Cordilleran Orogen: Conterminous U.S., The Geology of North America, Vol. G-3, *DNAG Series, Geol. Soc. of America*, Boulder, U.S., pp. 261-406.

Clark, A.H., Mayer, A.E.S., Mortimer, C., Sillitoe, R.H., Cooke, R.U. and Snelling, N.J., 1967 - Implications of isotopic ages of ignimbrite flows, southern Atacama Desert, Chile: *Nature*, v. 215, pp. 3-17.

Clark, A.H., Tosdal, R.M., Farrar, E. and Plazolles, V.A., 1990 - Geomorphologic environment and age of supergene enrichment of the Cuajone, Quellaveco, and Toquepala porphyry copper deposits, southern Peru: *Economic Geology,* v. 85, pp. 1604-1628.

Clauer, N. and Chaudhuri, S., 1995 - Clays in Crustal Environments; Isotope Dating and Tracing*;* *Springer-Verlag,* Berlin, 359p.

Cook, S.S., 1988 - Supergene copper mineralization at the Lakeshore Mine, Pinal County, Arizona*:* *Economic Geology,* v. 83, pp. 297-309.

Cook, S.S., 1988b - Petrologic studies of the supergene copper mineralization at the Santa Cruz porphyry copper deposit, Pinal County, Arizona: *Geological Society of America* Abstracts with Programs, p. A336.

Cook, S.S., 1994 - Geologic History of Supergene Copper Mineralization in the Porphyry Copper Deposits of Southwestern North America: unpublished Ph.D. dissertation, *University of Arizona,* Tucson, 163p.

Corn, R.M., 1975 - Alteration-mineralization zoning, Red Mountain, Arizona: *Economic Geology,* v. 70, pp. 1437-1447.

Creasey, S. C., 1967 - General Geology of the Mammoth Quadrangle, Pinal County, Arizona*: U.S. Geological Survey* Bull. 1218, 94p.

Creasey, S.C., 1980 - Chronology of intrusion and deposition of porphyry copper ores, Globe-Miami District, Arizona: *Economic Geology,* v. 75, pp. 830-844.

Creasey, S.C. and Kistler, R.W., 1962 - Age of some copper-bearing porphyries and other igneous rocks in southeastern Arizona: *U.S. Geological Survey* Professional Paper 450-D, pp. D1-D5.

Cummings, R.B., 1982 - Geology of the Sacaton porphyry copper deposit: *in* Titley, SK, (Ed.), Advances in Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 507-521.

Damon, P.E., Shafiqullah, M. and Leventhal, J.S., 1974 - K-Ar geochronology for the San Francisco volcanic field and rate of erosion of the Little Colorado River: in Geology of Northern Arizona, Part 1, Regional studies, Guidebook, *Geol. Soc. America* Rocky Mountain Section meeting, Flagstaff, p. 221.

Damon, P.E., Lynch, D.J. and Shafiqullah, M., 1984 - Cenozoic landscape development in the Basin and Range Province of Arizona: *in* Smiley, T.L., and others, (Eds.), Landscapes of Arizona - The Geological Story: Lanham, M.D., *University Press of America,* pp. 175-227.

Davis, G.H., 1979 - Laramide folding and faulting in southeastern Arizona: *American Journal of Science*, v. 279, pp. 543-569.

de Cserna, Z., 1989 - An outline of the geology of Mexico; *in* Bally, A.W. and Palmer, A.R., (Eds.) 1989, The Geology of North America: An Overview Vol. A, *DNAG Series, Geol. Soc. of America*, Boulder, U.S., pp. 261-406.

Dixon, D.W., 1966 - Geology of the New Cornelia Mine, Ajo, Arizona; *in* Titley, S.R. and Hicks, C.L., (Eds.), 1966, Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 123-132.

DuHamel, J.D., Cook, S.S., and Kolessar, L, 1995 - Geology of the Tyrone porphyry copper deposit, New Mexico: *Arizona Geological Society* Digest 20, pp. 464-472.

Eberly, L.D. and Stanley, T.B., Jr., 1978 - Cenozoic stratigraphy and geologic history of southwestern Arizona: *Geol. Soc. Am.* Bull., v. 6, pp. 921-940.

Einaudi, T.M, 1982 - Description of skarn associated with porphyry copper plutons; *in* Titley, S.R., (Ed.), 1982, Advances in Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 139-183.

Emmons, W.H., 1917 - The Enrichment of Ore Deposits: *U.S. Geological Survey* Bulletin 625, 530p.

Force, E.R., 1997 - A new Mid-Tertiary unit in the Ajo district, southern Arizon, and implications for extensional history: *in* Richard, S.M., (Ed.), Field Guide, Quitovac, Sonora and Ajo, Arizona, Guidebook for the *Arizona Geological Society* Spring Field Trip, March 22-23, 1997, pp. 23-28.

Gilluly, J., 1937 - Geology and Ore Deposits of the Ajo Quadrangle, Arizona: *Arizona Bureau of Mines* Bulletin 141, 83p.

Gilluly, J., 1946 - The Ajo Mining District: *U.S. Geological Survey* Professional Paper 209, 112p.

Gilmour, P., 1995 - A field guide to leached capping interpretation: *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995, Porphyry Copper Deposits of the American Cordillera; *Arizona Geol. Soc.* Digest 20, pp. 169-179.

Glassman, J.R., Larter, S., Briedis, N.A. and Lundegard, P.D., 1989 - Shale diagenesis in the Bergen High area, North Sea: *Clays and Clay Minerals,* v. 37, pp. 97-112.

Graybeal, F.T., 1982 - Geology of the El Tiro Area: *in* Titley, SK, (Ed.), Advances in Geology of the Porphyry Copper Deposits, Southwestern North America: *University of Arizona Press*, Tucson, pp. 487-505.

Gustafson, L.B. and Hunt, J.B., 1975 - The porphyry copper deposit at El Salvador, Chile: *Economic Geology,* v. 70, pp. 857-912.

Hagstrum, L.T., Cox, D.P. and Miller, R.L, 1987 - Structural reinterpretation of the Ajo Mining District, Pima County, Arizona, based on paleomagnetic and geochronologic studies: *Economic Geology,* v. 82, pp. 1348-1361.

Heidrick, T.L. and Titley, S.R., 1982 - Fracture and dike patterns in Laramide plutons and their structural and tectonic implications; *in* Titley, S.R., (Ed.), 1982, Advances in Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 73-92.

Heindl, L.A., 1963 - Cenozoic Geology in the Mammoth Area, Pima County, Arizona: *U.S. Geological Survey* Bull. 1141-E, 41p.

Hemon, R.M. and Jones, W.R., 1968 - Ore deposits of the

Central Mining District, Grant County, New Mexico: *in* Ridge, J.D., (Ed.), Ore Deposits of the United States 1933-1967: *American Inst. of Mining Metallurgical, and Petroleum Engineers, Inc*., New York, pp. 1212-1236.

Huff, L.C., 1970 - A geochemical study of alluvium-covered copper deposits in Pima County, Arizona*: U.S. Geological Survey* Bulletin 1312-C, pp. Cl -C32.

Kemp, J.F., 1905 - Secondary enrichment of ore-deposits of copper: *Economic Geology*, v. 1, pp. 11-15.

King, J.R., 1982 - Geology of the San Xavier North porphyry copper deposit: *in* Titley, S.R., (Ed.), 1982, Advances in Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 475-485.

Kreis, H.G., 1995 - Geology of the Santa Cruz porphyry copper deposit: *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995, Porphyry Copper Deposits of the American Cordillera; *Arizona Geol. Soc.* Digest 20, pp. 364-365.

Langton, J.M., 1973 - Ore genesis in the Morenci-Metcalf District: *Society of Mining Engineers* Transactions, v. 254, pp. 247-257.

Lindgren, W., 1905 - The copper deposits of the Clifton-Morenci district, Arizona: *U.S. Geological Survey* Professional Paper 43, 375p.

Livingston, D.E., Damon, P.E., Mauger, R.L., Bennet, R. and Laughlin, A.W., 1967 - Argon-40 in cogenetic feldspar-mica assemblages: *Jour. Geophys. Research,* v. 72, p. 1361.

Livingston, D.E., Mauger, R.l. and Damon, P.E., 1968 - Geochronology of the emplacement, enrichment and preservation of Arizona porphyry copper deposits: *Economic Geology,* v. 63, pp. 30-36.

Locke, A., 1926 - Leached Outcrops as Guides to Copper Ore: *Williams and Wilkins*, Baltimore, 175p.

Loghry, J.D., 1972 - Characteristics of favourable cappings from several southwestern porphyry copper deposits: Unpub. M.S. thesis, *University of Arizona*.

Long, K.R., 1995 - Production and reserves of the Cordilleran (Alaska to Chile) porphyry copper deposits: *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995, Porphyry Copper Deposits of the American Cordillera; *Arizona Geol. Soc.* Digest 20, pp. 35-68.

Lopez, J.A. and Titley, S.R., 1995 - Outcrop and capping characteristics of the supergene sulphide enrichment at North Silver Bell, Pima County, Arizona: *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995,. Porphyry Copper Deposits of the American Cordillera; *Arizona Geol. Soc.* Digest 20, pp. 424-435.

Lovering, T.S., Huff, L.S. and Almond, H., 1950 - Dispersion of copper from the San Manuel copper deposit, Pinal. County, Arizona: *Economic Geology,* v. 45, pp. 493-514.

Melchiorre, E.B. and Enders, M.S., 2003 - Stable isotope geochemistry of copper carbonates at the Northwest Extension Deposit, Morenci district, Arizona: *Economic Geology,* v. 98, pp. 697-621.

Miller, D.M., Nilsen, T.H. and Bilodeau, W.L., 1992 - Late Cretaceous and early Eocene geologic evolution of the U.S. Cordillera; *in* Burchfiel, B.C., Lipman, P.W. and Zoback, M.L., (Eds.) 1992, The Cordilleran Orogen: Conterminous U.S., The Geology of North America, Vol. G-3, *DNAG Series, Geol. Soc. of America*, Boulder, U.S., pp. 205-260.

Moolick, R.T. and Durek, J.J., 1966 - The Morenci District; *in* Titley, S.R. and Hicks, C.L., (Eds.), Geology of the Porphyry Copper Deposits, Southwestern North America: *University of Arizona Press,* Tucson, pp. 221-231.

Mortimer, C., 1973 - The Cenozoic history of the southern Atacama Desert, Chile*: Geological Society of London Journal,* v. 129, pp. 505-526.

Mortimer, C., Munchmeyer, F.C. and Urqueta, D.I., 1977 - Emplacement of the Exotica orebody, Chile*: Inst. Mining Metallurgy.* Trans., sec. B, pp. B121 - B127.

Mote, T.I. and Brimhall, G.H., 1997 - Linking secondary mineralization at El Salvador, Chile to Middle Miocene climate transitions by geochronology and mass balance: *Geol. Soc. America,* Abstracts with Program 1997, Salt Lake City, p. A-17.

Mutschler, F.E., Ludington, S. and Bookstrom, A.A., 2000 - Giant porphyry-related metal camps of the world - a database; U.S. Geological Survey Open-File Report 99-556, Online Version 1.0, http://geopubs.wr.usgs.gov/open-file/of99-556/world_ppy.xls

Nations, D., Wilt, J.C. and Hevly, R.H., 1985 - Cenozoic paleogeography of Arizona: *in* Flores, R.M., and Kaplan, S.S., (Eds.), Cenozoic Paleogeography of the West-Central United States, Rocky Mountain Paleogeography Symposium 3; *Soc. Econ. Paleo. and Minera.*, pp. 335-355.

Oldow, J.S., Bally, A.W., Avé Lallemant, H.G. and Leeman, W.P., 1989 - Phanerozoic evolution of the North American Cordillera; United States and Canada; *in* Bally, A.W. and Palmer, A.R., (Eds.) 1989, The Geology of North America: An Overview Vol. A, *DNAG Series, Geol. Soc. of America*, Boulder, U.S., pp. 139-232.

Olmstead, H.W. and Johnson, D.W., 1966 - Inspiration geology: *in* Titley, S.R. and Hicks, C.L., (Eds.), Geology of the Porphyry Copper Deposits, Southwestern North America: *University of Arizona Press,* Tucson, pp. 143-150.

Parsons, A.B., 1933 - The porphyry coppers: *American Institute of Mining and Metallurgical Engineers*, New York, 581p.

Paige, S., 1922 - Copper Deposits of the Tyrone District, New Mexico: *U.S. Geological Survey* Professional Paper 122, 53p.

Peterson, N.P., 1962 - Geology and Ore Deposits of the Globe-Miami District, Arizona: *U.S. Geological Survey* Professional Paper 342, 151p.

Preece, R.K., 1989 - Geology and mineralization of the Northwest Extension - summary of activities during 1988: Unpublished project report, *Phelps Dodge, Morenci Inc.,* Phoenix, Arizona. 336p.

Ransome, F.L., 1904 - Geology and Ore Deposits of the Bisbee Quadrangle: *U.S. Geological Survey* Professional Paper 21, 168p.

Rehrig, W.A. and Heidrick, T.L., 1972 - Regional fracturing in Laramide stocks in Arizona and its relationship to porphyry copper mineralization: *Economic Geology,* v. 67, pp. 198-213.

Riggs, N.R., Hon, K.A. and Haxel, G.B., 1994 - Early to Middle Jurassic magmatic arc rocks of south-central and southeastern Arizona; *in* Thorman, C.H. and Lane, D.E. (Eds.), 1994, USGS Research on Mineral Resources - 1994, Part B - Guidebook for Field Trips, Ninth V.E. McKelvey Forum on Mineral and Energy Resources, *U.S. Geological Survey Circular* 1103-B, pp. 7-11.

Rose, A.W. and Baltosser, W.W., 1966 - The porphyry copper deposit at Santa Rita, New Mexico; *in* Titley, S.R. and Hicks, C.L., (Eds.), 1966, Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 205-220.

Sandbak, L.A. and Alexander, G.H., 1995 - Geology and rock mechanics of the Kalamazoo orebody, San Manuel, Arizona; *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995, Porphyry Copper Deposits of the American Cordillera: *Arizona Geol. Soc.* Digest 20, pp. 396-423.

Scarborough, R.B., 1989 - Cenozoic erosion and sedimentation in Arizona: *in* Jenney, L.P. and Reynolds, S.J., (Eds.), Geologic Evolution of Arizona: *Arizona Geological Society* Digest 17, pp. 515-537.

Schwartz, G.M., 1949 - Oxidation and enrichment in the San Manuel copper deposit, Arizona*: Economic Geology,* v. 44, pp. 253-277.

Schwartz, G.M., 1953 - Geology of the San Manuel copper deposit, Arizona; *U.S. Geological Survey* Professional Paper 256, 63p.

Segerstrom, K., 1963 - Mature land of northern Chile and its relation to ore deposits: *Geol. Soc. America* Bull., v. 74, pp. 513-518.

Shafiqullah, M., Damon, P.E., Lynch, D.J., Reynolds, S.J, Rehrig, W.A. and Raymond, R.H., 1980 - K-Ar geochronology and geologic history of Southwestern Arizona and adjacent areas*: Arizona Geological Society* Digest, Volume XII, pp. 201-260.

Sillitoe, R.H., Mortimer, C. and Clark, A.H., 1968 - A chronology of landform evolution and supergene mineral alteration, southern Atacama Desert, Chile: *Inst. Mining and Metallurgy* Trans., sec. B, v. 77, pp. B166-B169.

Sillitoe, R.H. and McKee, E.H., 1996 - Age of Supergene Oxidation and Enrichment in the Chilean Porphyry Province: *Economic Geology,* v. 91, pp. 164-179.

Somers, R.E., 1915 - Geology of the Burro Mountains copper district, New Mexico: *American Institute of Mining Engineering* Transactions, v. 43, pp. 240-290.

Spencer, J.E., Richard, S.M., Reynolds, S.J., Miller, R.J, Shafiqullah, M., Gilbert, W.G. and Grubensky, M.J., 1995 - Spatial and temporal relationships between Mid-Tertiary magmatism and extension in southwestern Arizona: *J. Geophys. Res.*, v. 100, no. B7, pp. 10321-10351.

Stewart, C.A., 1912 - The geology and ore deposits of the Silver Bell Mining District, Arizona: *AIME Transactions*, v. 43, pp. 240-290.

Stokes, H.N., 1906 - Experiments on the solution, transportation, and deposition of copper, silver, and gold: *Economic Geology*, v. 1, pp. 644-660.

Sullivan, E.C., 1905 - The chemistry of ore-deposition, precipitation of copper by natural silicates; *Economic Geology*, v. 1 pp. 67-73.

Thomas, L.A., 1966 - Geology of the San Manuel ore body; *in* Titley, S.R. and Hicks, C.L., (Eds.), 1966, Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 133-142.

Titley, S.R., 1981 - Geologic and geotectonic setting of porphyry copper deposits in the southern Cordillera: *in* Dickinson, W.R. and Payne, W.D., (Eds.), 1981, Relations of Tectonics to Ore Deposits in the Southern Cordillera; *Arizona Geol. Soc.* Digest 14, pp. 79-98.

Titley, S.R., 1982 - Geologic setting of porphyry copper deposits; *in* Titley, S.R., (Ed.), 1982, Advances in Geology of the Porphyry Copper Deposits, Southwestern North America; *University of Arizona Press,* Tucson, pp. 37-58.

Titley, S.R., 1982a - Some features of the tectonic history and ore genesis in the Pima Mining District; *in* Titley, S.R., (Ed.), 1982, Advances in Geology of the Porphyry Copper Deposits, Southwestern North America; The *University of Arizona Press,* Tucson, pp. 387-486.

Titley, S.R., 1993 - Characteristics of porphyry copper occurrences in American southwest: *in* Kirkham, R.V., Sinclair, W.D., Thorpe, R.I. and Duke, J.M., (Eds.), 1993, Mineral Deposits Modelling: *Geological Association of Canada,.* Special Paper 40, pp. 433-464.

Titley, S.R., 1994 - An abridged overview of some features of porphyry copper deposits in the American southwest; *in* Thorman, C.H. and Lane, D.E. (Eds.), 1994, USGS Research on Mineral Resources - 1994, Part B - Guidebook for Field Trips, Ninth V.E. McKelvey Forum on Mineral and Energy Resources, *U.S. Geological Survey Circular* 1103-B, pp. 15-23.

Titley, S.R., 1995 - Geological summary and perspective of porphyry copper deposits in southwestern North America: *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995, Porphyry Copper Deposits of the American Cordillera: *Arizona Geol. Soc.* Digest 20, pp. 6-20.

Titley, S.R., Anzalone, S.A. and Anthony, E.Y., 1989 - Porphyry copper deposits in the American southwest - IGC Field Trip T338; *in* Titley, S.R., (Leader), Porphyry copper deposits in the

American southwest, Field Trip Guidebook T338. Part of Mineral Deposits of North America, 28th Int Geol Cong, *American Geophysical Union,* Washington, pp. T338:1-26.

Titley, S.R. and Marozas, D.C., 1995 - Processes and products of supergene copper enrichment: *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995, Porphyry Copper Deposits of the American Cordillera: *Arizona Geol. Soc.* Digest 20, pp. 156-168.

Vasconcelos, P.M., Brimhall, G.H., Becker, T.A., and Renne, P.R., 1994 - $^{40}Ar/^{39}Ar$ analysis of supergene jarosite and alunite: Implications to the paleoweathering history of the western USA and West Africa: *Geochim et Cosmochim Acta,* v. 58, pp. 401-420.

Weiss, R.L., 1965 - Outcrops as guides to copper ore - Four examples: Unpublished Phd dissertation, *Columbia University*

Wilkins, J. and Heidrick, T.L., 1995 - Post Laramide extension and rotation of porphyry copper deposits, southwestern United States: *in* Pierce, F.W. and Bolm, J.G., (Eds.), 1995. Porphyry Copper Deposits of the American Cordillera; *Arizona Geol. Soc.* Digest 20, pp. 109-127.