THE EVOLUTION OF SUPERGENE ENRICHMENT IN THE MORENCI
PORPHYRY COPPER DEPOSIT, GREENLEE COUNTY, ARIZONA

by

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Merritt Stephen Enders

The Evolution of Supergene Enrichment in the Morenci

Porphyry Copper Deposit, Greenlee County, Arizona

Doctor of Philosophy
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ACKNOWLEDGEMENTS

This work was initiated because I started a conversation with Dr. P.J Ryan, executive vice president of Phelps Dodge Mining Company, over a beer at the company’s guesthouse in Clifton in May 1994. I invited him to spend a day in the field, unencumbered by meetings, just to review the geology of the district. So many questions came up during our trip, that Pat suggested we find a student to support for some basic geologic research. I spent the five following months looking for such a student but came up empty handed. At the time, I was the Chief Geologist at Morenci, which was mostly an administrative job, and frustrated by not having the time to study the geology of this world class copper deposit. In January 1995, I met with T.R. Snider, president of Phelps Dodge Morenci Inc, and volunteered to go back to school and conduct some research myself. When Tim said he thought that was a good idea, I almost fell over. Today, six years after my initial conversation, I am profoundly grateful to P.J. Ryan, T.R. Snider, J.S. Whisler, A.L. Lawrence, H.M. Conger, W.H. Wilkinson, M.W. Bartlett, and R.J. Stegen for the opportunity and support to study the Morenci district. I feel great about the legacy I leave behind and the experience that I will always carry with me. Thank you.

There were expectations associated with this opportunity, however. Not only was I expected to conduct original scientific research from an academic perspective, I was also expected to create value for Phelps Dodge. So, I decided to study supergene mineralization, because of its significant economic impact to the company and myriad of unanswered research questions. To do this, I designed a broad, multi-disciplinary research program to look for evidence at scales from the regional to the microscopic using multiple analytical methods. To get the job done, I leveraged my time and resources by collaborating with a number of other researchers. Charles Ferguson of the Arizona Geological Survey and David Parker of Phelps Dodge contributed their time and expertise on the revised geologic map of the Clifton-Morenci area. Spence Titley provided encouragement, advice, insight, and energy for the detailed study of the supergene mineralization; and when there were no obvious answers, he consoled me by sitting on the muck pile and saying, “God just made it that way.” Gordon Southam and Chris Knickerbocker of the Department of Biosciences at Northern Arizona University opened up the world of bacteria/mineral interactions and provided important laboratory support. Gentlemen, without your help, this study would not have been possible, thank you.

There were so many others who contributed to this work and I have tried to acknowledge your help in the text. If I have missed someone, please accept my apologies and know that I am grateful. I would particularly like to thank Roberto Sotelo and Linda Dufek for their help in preparing the figures, Mark Hertel for help with the Medsystem modeling, Tim Orr for the digital cartography, Wes Bilodeau for use of the XRD lab, Ralph Stegen, Bob North and David Parker for the edits, and Mark Barton, Joaquin Ruiz and Bill Chavez for the advice. Finally, I would like to thank Sydney and Maegan for their understanding, support and encouragement to fulfill my dreams.
DEDICATION

I stand on the shoulders of giants. The hard work and dedication of the geologists
who have worked at Morenci and studied the geology of this great district over the last 100
years was of fundamental importance in establishing our understanding today. The careful
and thorough documentation of their observations and interpretations has been extremely
helpful. So, I would like to dedicate this dissertation to the geologists who have come
before us, to those of you working at Morenci today, and to the next generation of
geoscientists to study the district. I have tried to respect and acknowledge the work that
has already been done, to give credit and thanks to those of you who have helped me during
my residence, and to leave behind a record of my work and ideas for your use in the future.
Best wishes and good prospecting. Yabadabado!
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ABSTRACT

Supergene enrichment in the Morenci porphyry copper deposit was formed as a result of the coupled processes of erosion and chemical weathering that accompanied five stages of landscape evolution in the Cenozoic Era. During Stage 1 (64 to 53 Ma), low-grade primary chalcopyrite and pyrite mineralization was deposited as a result of Laramide magmatic and hydrothermal processes at about 55 Ma. During Stage 2 (53 to 30 Ma), initial unroofing and erosion removed approximately 1.8 km of rocks overlying the deposit and shed detritus to the north in the Eocene and to the south in the early Oligocene. During Stage 3 (30 to 18 Ma), the deposit was preserved under 640 to 950 meters of volcanic rocks as a result of mid-Tertiary extension and volcanism. During Stage 4 (18 to 2 Ma), most of the supergene copper enrichment at Morenci appears to have been formed as a result of Basin and Range deformation between ~13 and ~4 Ma. Sixteen new $^{40}$Ar/$^{39}$Ar ages from alunite, jarosite, and potassium-bearing manganese oxides in the district recorded three cycles of enrichment and leaching that peaked at about 7.3 Ma. Microbiological and geological studies revealed that acidophilic iron oxidizing bacteria and dissimilatory sulfate reducing bacteria contributed to leaching and enrichment of copper in the supergene environment, at least since the late Miocene. During Stage 5 (2 Ma to present), destruction of the current enriched blanket accompanied base-level drop and stream incision as a result of progressive drainage integration in southern Arizona in the late Pliocene and Pleistocene.
INTRODUCTION

The Morenci district in southeastern Arizona (Figure 1) contains one of the largest supergene porphyry copper deposits in the world and is an excellent site to study supergene processes. Although the district was structurally disturbed and dissected because of mid-Tertiary extension and Basin and Range deformation, the Morenci porphyry copper deposit appears to be relatively intact. During the last two decades, over 300,000 meters (about 1 million feet) of exploration and development drilling in over 2,000 new drill holes have been completed along with geologic mapping, metallurgical testing and other related studies to support exploration and operations. We now recognize that the deposit contains a laterally continuous enrichment profile that is over 600 m (almost 2,000 ft) thick and covers over 19 km² (7.5 mi²) that encompasses the Morenci, Metcalf, Northwest Extension, Southside, Coronado, Western Copper, Garfield, Shannon, American Mountain, Fairbanks, and adjacent areas (Figure 1). Mining and exploration during the last 60 years have resulted in a wide variety of exposures in outcrop and drill core. These range from un-mined leached capping at the surface to deep exposures of the base of the supergene blanket and underlying hypogene zone across a composite vertical profile of over 1,650 m (5,400 ft). This situation provides an exceptional opportunity to study an unparalleled view of a world class orebody.

Morenci is truly a world class copper deposit (Figure 2). In sheer size, only La Escondida exceeds the Morenci supergene deposit. Reported past production and published reserves for Morenci total more than 6.7 Btons, at an average grade of 0.42%
Cu, that contain approximately 28 Mtons of copper (Table 1). Almost all of this copper is from supergene enrichment of hypogene copper mineralization. Underground mining of high-grade copper oxide deposits began in 1872, followed by open-pit mining, conventional milling, and froth flotation recovery from the rich sulfide mineralization in the original Clay deposit in 1937 (Moolick and Durek, 1966). By 1987, Phelps Dodge Mining Company had initiated dump leaching and Solvent Extraction / Electrowinning (SX/EW) operations to recover copper from existing low-grade ores and stockpiles as well as from oxide mineralization in the district. In 1999, Phelps Dodge produced over 450,000 metric tons of copper from supergene sulfide and oxide ores that were mined in the Metcalf, Northwest Extension, Southside, and Coronado areas (Figure 1).

The economics of leaching and SX/EW operations have lowered the cutoff grade for some materials down to 0.10% Cu or only 1,000 PPM, which resulted in significant expansions to the limits and continuity of mineralization since 1993. Understanding the distribution and character of supergene mineralization is therefore very important from an economic perspective. This district-wide geologic perspective has provided new insights into the scale, timing, and processes that define the supergene environment at Morenci, and is the focus of this study.

**Study Site**

Location and Physiography

The Morenci district is located in the Transition Zone physiographic province of Arizona on the southern flank of the White Mountains and at the northern end of the Duncan
basin (Figure 3). The topography of the area is very rugged and contains mountainous areas with steep cliffs and deeply incised canyons in the adjacent valleys. Elevations average about 1,700 meters (5,575 ft) above sea level and range from a high of about 2,100 (6,890 ft) meters in the north to a low of about 1,035 meters (3,395 ft) in the south. The district is located in the Gila River drainage basin and is partially surrounded by three perennial streams: the Gila River, Eagle Creek, and the San Francisco River (Figure 3). Prior to mining, Chase Creek and its tributaries formed a southerly-flowing intermittent stream drainage system that occupied an axial position through the center of the district. As a result, there are strong topographic and hydrologic gradients that have affected the supergene environment and processes at Morenci.

Hydrogeology

The hydrogeologic system in the Morenci sub-basin is characterized almost entirely by fracture flow in consolidated bedrock (Dames and Moore, 1995). Groundwater originates as infiltration from rainfall and snowmelt in the higher elevations of the basin, and flows toward the lower elevations where it appears as springs and provides underflow to perennial streams. Groundwater elevations tend to follow topography and are highest in the northern part of the district and lowest near the perennial streams on the eastern, southern, and western boundaries of the district (Figure 4). Groundwater has a near-neutral pH and is dominated by calcium and sulfate, with lower concentrations of sodium/potassium, chloride, magnesium, and carbonate/bicarbonate (Dames and Moore, 1995). Groundwater depths range from about 80 m (260 ft) to over 260 m (850 ft) below
the pre-mine topography (Dames and Moore, 1995). As a result, there are significant thicknesses of unsaturated rock above the vadose zone, and the modern water table cuts across a variety of mineralogical and hydrochemical environments in the supergene zone.

Climate and Weather

The climate of the Morenci district is semi-arid and typical of the Mexican Highland portion of the Basin and Range where a wide range of conditions exist that are directly linked to variations in altitude and geomorphology. Average daily minimum and maximum temperatures for the region are –5° to 15°C in January and 17° to 35°C in July (Remick, 1989). Annual precipitation at Morenci has averaged 33 cm (13 in) over the last 43 years (Phelps Dodge, 1996a) while the lake evaporation rate in the Duncan valley is about 15 to 17 cm (5.9 to 6.7 in) per year (Anderson, et. al., 1992). Most of the precipitation occurs in two periods: in July, August, and September during the annual monsoon season, and in December through February from winter storms (Figure 5). It is likely there have been strong, local, seasonal, warm to cold and wet to dry cycles which have affected the supergene environment at Morenci as well as regional/global climate changes during the Cenozoic era.

Previous Work

Morenci District

A number of people have studied the geology of the Morenci district over the last 125 years. Raymond (1874) was the first to mention the mining potential, and Wendt
(1887) was the first to describe the geology of the district. Waldemar Lindgren (1905a) published the first comprehensive descriptions of the district in U.S.G.S. Professional Paper No. 43 and the Clifton Folio (1905b). Tolman (1909), Reber (1916), Butler and Wilson (1938), and Schwartz (1947) added their observations and interpretations to the record over the next several decades. Moolick and Durek (1966) published an update on Morenci in the Geology of the Porphyry Copper Deposits. A few years later, Langton (1973) added his interpretation of the geologic evolution of the district and Bennett (1975) studied the geology and origin of the breccias in the district. The modern era of geologic investigation began in the 1980’s with the work of Menzer (1980), Pawlowski (1980a, b), Preece (1981, 1984, 1986, 1989), and Preece and Menzer (1982, 1992). This work continued in the 1990’s by many of their talented co-workers (Griffin, Ring, and Lowery, 1993; North and Preece, 1993; Preece, Stegen, and Weiskopf, 1993; Walker and Pawlowski, 1993; Walker, 1995; Calkins, 1997; Cheff et al., 1997; Parker and Calkins, 1997; Pawlowski et al., 1997; Wright, 1997; Holick, 1998; Young-Mitchell et al., 1998, 1999). Unfortunately, most of this work resulted in internal Phelps Dodge company reports or unpublished extended abstracts from field trips, short courses, and conferences. Thus the published record of the geology of the Morenci deposit has been relatively fragmented and incomplete over the last 25 years. Professional Paper No. 43 remains the landmark geologic publication on the geology of the district even today.
Supergene Enrichment

Various people have studied the geology of supergene copper deposits since S.F. Emmons (1900) and W.H. Emmons (1913, 1917) wrote their extensive descriptions of enriched ores in many of the mining districts of the United States. Lindgren (1905a) was the first to provide a detailed description of supergene copper deposits when he studied the Morenci district. The interpretation of leached outcrops in southwestern North America has been well studied by several geologists including Locke (1926), Weiss (1965), Blanchard (1968), Loghry (1972) and J. A. Anderson (1982). Oxidation and enrichment processes have been studied and described by many geologists over the past 100 years. Kemp (1905), Sullivan (1905), Stokes (1906), Garrels (1954), Charles Anderson (1955), Garrels and Thompson (1960), Sato (1960a,b, 1992), Sato and Mooney (1960), Durek (1964), and Bladh (1982) have done the most notable work to this time. Posnjak and Merwin (1922), and Tunell and Posnjak (1931) reported basic iron-sulfur-water chemistry.

Over the last 15 years, studies of supergene copper enrichment have expanded to include modern geochemical methods and computer modeling approaches in combination with classic field and laboratory observations. Sikka et al. (1991) conducted detailed studies of supergene enrichment and oxidation at Malanjkhand, India and reported detailed observations and possible reactions for a large variety of secondary copper minerals. Brimhall et al. (1985) were the first to use mass balance calculations from drill hole profiles and groundwater solute transport models to predict copper fluxes and to reconstruct paleosurficial topography. Several other studies followed that included mass
balance considerations, K-Ar geochronology of alunites, paleotopographic reconstruction, and climatic factors (Alpers and Brimhall, 1988, 1989; Sillitoe and McKee, 1996). During this time, Ague and Brimhall (1989), Lichtner and Biino (1992), and Lichtner (1994) used numerical simulation and advective solute transport methodology to model supergene enrichment characteristics and calculated mineral profiles. Vasconcelos et al. (1994a,b) further developed the application of $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology to dating alunites, jarosites and potassium-bearing manganese oxide minerals in weathering profiles in the western United States, West Africa, and South America. Cook (1994) used K-Ar geochronology of alunite and illite in 15 porphyry copper deposits in southwestern North America and developed a geologic history of supergene enrichment for the region. Most recently, Mote and Brimhall (1997, 1998a,b) and Mote et al. (1999a,b) have combined mass balance calculations with $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of transported alunites and manganese oxide minerals to examine copper fluxes in exotic ores at El Salvador, Chile.

**Classic Concepts of Supergene Enrichment**

The papers by Titley and Marozas (1995) and J.A. Anderson (1982) provide an excellent summary of the processes and products of supergene enrichment that serves as a template for examining enrichment profiles (Figure 6, Table 2). Enrichment in porphyry copper deposits starts when typically low-grade (0.05% to 0.35% Cu) primary pyrite and chalcopyrite mineralization is exposed to oxygenated groundwaters. This process typically requires pyrite-to-chalcopyrite contents $>4:1$ (Titley and Marozas, 1995). In this case, oxidation of pyrite in the vadose zone and capillary fringe above the water table forms
sulfuric acid and ferric sulfate that react completely with chalcopyrite to form soluble cupric sulfate and ferrous sulfate. This process leaves behind a “leached capping” that is typically devoid of copper and contains a mixture of the iron oxide and sulfate minerals hematite, goethite, and jarosite which comprise the classic limonite assemblage (Blanchard, 1968; J.A. Anderson, 1982). Where this process is incomplete, a zone of “partial leaching” is left behind beneath the leached capping. The copper in solution migrates downward to a redox (reduction/oxidation) boundary at or below the water table where it reacts with the reduced sulfur in chalcopyrite and pyrite and forms secondary copper sulfides in an “enriched blanket”. Downward zoning of secondary copper sulfides reflects changing Eh-pH conditions and solution chemistry that yields a suite of secondary copper minerals with variable copper to sulfur ratios. This mineral suite can include: chalcocite (Cu$_{2.00}$S - cc), djurleite (Cu$_{1.96}$S - dj), digenite (Cu$_{1.80}$S - dg), anilite (Cu$_{1.75}$S - an), geerite (Cu$_{1.60}$S - ge), spionkopite (Cu$_{1.39}$S - sp), yarrowite (Cu$_{1.13}$S - ya), covellite (Cu$_{1.00}$S - cv), idaite (Cu$_3$FeS$_4$ - id), and bornite (Cu$_5$FeS$_4$ - bn) as a series of replacements of each other and of chalcopyrite and pyrite (Sikka et al., 1991). Secondary copper minerals follow the Schurmann Series (Lindgren, 1933) and preferentially replace sphalerite before chalcopyrite, and chalcopyrite before pyrite. Replacement textures range from complete volume-for-volume replacement to thin coatings on grain boundaries. Early cycle leaching and enrichment processes typically result in an enrichment of copper grade by a factor of at least 2x. For example, complete replacement of chalcopyrite by chalcocite (CuFeS$_2$ \( \rightarrow \) Cu$_2$S) yields an enrichment factor of 2.3.
This process is cyclical and reflects episodic vertical changes in the position of the redox boundary as a result of tectonic, physiographic, and climatic changes (Figure 6). Subsequent cycles of erosion and weathering continue to dissolve copper minerals above the water table and both enrich and thicken the successive blankets with time (Brimhall et al., 1985). Where there is sufficient pyrite remaining (3:1 py:cc), dissolution of chalcocite in a former enriched blanket leaves behind a mixture of typically transported hematite and goethite (Table 2) (Titley and Marozas, 1995). Where the pyrite content is lower (1:2 py:cc), dissolution of chalcocite yields classic and distinctive hematite boxworks (Titley and Marozas, 1995; J.A. Anderson, 1982). Where there is insufficient pyrite to oxidize and mobilize copper from either secondary or primary minerals or in the presence of acid-consuming wall rocks such as limestones, skarns, or feldspar and biotite-bearing intrusive rocks, the minerals are oxidized in-situ with only minor transportation of copper. This results in a complex assemblage of copper oxide minerals including chalcocite, brochantite, tenorite, cuprite, native copper, malachite, azurite, chrysocolla and a number of other secondary oxide minerals depending on Eh, pH, \( P_{\text{CO}_2} \), \( P_{\text{O}_2} \), \( [\text{SO}_4^{2-}] \) and a variety of other environmental and geochemical conditions. Late cycle leaching and enrichment processes typically result in an enrichment of copper grade by factors over 5x by replacement of both chalcopyrite and pyrite.

Alteration of K-Al silicate minerals in the host rocks typically accompanies supergene enrichment (Table 2). The reactions during supergene enrichment are the same as typical acid weathering (Titley and Marozas, 1995). This involves the conversion of feldspar to muscovite or muscovite to kaolinite. White supergene kaolinite is ubiquitous in
the supergene profiles in felsic porphyry copper systems with abundant hypogene quartz and sericite alteration. In extreme acid systems, this process can liberate alumina to form “alum” (Titley and Marozas, 1995). Acids formed by the dissolution of pyrite also react with K-Al silicate host rocks to produce alunite and jarosite (Table 2) under high acid and sulfate conditions (Bladh, 1982). Both alunite and jarosite are conspicuous products of the oxidation and leaching cycles in some of the supergene porphyry copper deposits of southwestern North America and the Southern Cordillera in Chile and Peru. Jarosite is a product of the immediate reaction of sulfates with K-bearing silicates, and alunite is mostly a product found beneath weathered, former enriched sulfide blankets (Titley and Marozas, 1995). From textural and petrographic evidence at La Escondida, Chile, Alpers and Brimhall (1988) concluded that supergene alunite formed beneath the water table in the relatively reducing zone. They further concluded that later descent of the oxidation front exposed the supergene alunite, and in some areas, there was sufficient ferric iron in solution to replace the alunite with jarosite. Because both alunite and jarosite contain potassium, they are amenable to radiometric age dating using K-Ar or $^{40}$Ar/$^{39}$Ar methods. They also contain four stable isotope sites, and complete analyses of $\delta^D$, $\delta^{18}O_{SO_4}$, $\delta^{18}O_{OH}$, and $\delta^{34}S$ can provide useful information about their environment of formation (Rye, et al., 1989, 1992, 1997, and 1998).

**Previous Notions of Supergene Enrichment at Morenci**

Supergene ores are of fundamental importance to the Morenci district and these have been studied since Lindgren (1905a) provided the first detailed descriptions. Since
then, a number of geologists have added to the understanding of supergene enrichment at Morenci including Moolick and Durek (1966), Langton (1973), North and Preece (1993), Cook (1994), Walker (1995), Enders et al., (1998a,b), Titley and Enders (1997, 1999), and Melchiorre and Enders (in prep). The studies contain some conflicting conclusions and show a progressive change in our understanding of the geology of the Morenci district and surrounding region.

Waldemar Lindgren’s (1905a) observations and interpretations from his work in Morenci formed part of the foundation of economic geology for nearly half a century thereafter. At the time, Lindgren considered the Morenci district to be a large group of separate deposits intimately associated with the porphyry intrusions. Lindgren divided the supergene profile into three zones: the “surface zone” or leached capping, the “chalcocite zone” or enriched blanket, and the “pyrite zone” or lower blanket/hypogene zone, in terms we use today. Lindgren concluded that most of the “great” north to northwest-striking faults and the bulk of the supergene enrichment at Morenci were formed prior to mid-Tertiary volcanism. He recognized that the deposits must have formed during a time when the water table was much higher than the modern one and thus concluded that the enriched deposits must have subsequently been stranded above the water table when the Morenci structural block was uplifted during “Gila Conglomerate time”. Although he did not emphasize a second period of enrichment, he did acknowledge that the deposits were subsequently re-exposed during late-Tertiary time to further oxidation and erosion. Lindgren further described the fault offsets and subsequent near-surface degradation of the enriched blanket and leached capping across the Copper Mountain fault as evidence of
mid-Tertiary enrichment. He concluded that the Chase Creek drainage was formed before
the “Gila Conglomerate” and used that as evidence for a “great age, slow oxidation, and
gradual erosion” of the Morenci deposits. Lindgren was the first to recognize that the
surface zone was formed from oxidation of the chalcocite zone instead of directly from the
pyrite zone, thus establishing the notion of multiple cycles or stages of enrichment at
Morenci.

Moolick and Durek (1966) provided an update on the geology of the Morenci
district focused on the Morenci and Metcalf areas. They also concluded that enrichment
formed during the mid-Tertiary, prior to late Tertiary volcanism and northwest faulting.
This was a significant departure from Lindgren’s interpretation of the timing of faulting.
Moolick and Durek mentioned a contact between oxidized ore and basalt, and proposed
that mid-Tertiary volcanic rocks had covered the deposit. They concluded that subsequent
weathering and canyon cutting were responsible for modifications to the supergene
deposits after the volcanic cover had been removed. They also recognized that “recent
erosion had cut drastically into the blanket”.

Langton (1973) was the first to take a district-wide approach to the study of
supergene enrichment at Morenci. He proposed a fairly explicit explanation for the
evolution of the supergene zone, although he provided little supporting evidence. Langton
also concluded that the bulk of enrichment was formed prior to mid-Tertiary volcanic
cover, but in two stages. This was consistent with the prevailing concepts of supergene
enrichment in the Southwest at the time (Livingston et al., 1968). The first stage was a
Late-Eocene period of erosion and leaching that formed a uniform bowl-shaped blanket
with an associated argillic alteration zone located in the central portion of the district. This was followed by a prolonged period of general uplift in the Oligocene that further oxidized and enriched the deposit and formed the leached capping prior to mid-Tertiary volcanism. He proposed that over 300 m (1,000 ft) of volcanic rocks covered the deposit and that this was associated with a swelling water table and lateral migration that resulted in “an even distribution of chalcocite over a 1,000-ft thickness during volcanism”. Langton attributed subsequent major uplift to Basin and Range deformation that caused major faulting and a rapid water table drop, formed an axial north to northwest-striking graben in the center of the district, and stranded the mature enrichment blanket. He suggested this led to the destruction of part of the blanket and produced immature, late Miocene to early Pliocene covellite and chalcocite enrichment of chalcopyrite. He further proposed that Basin and Range deformation stranded the Metcalf blanket 365 m (1,200 ft) above the Morenci blanket, and that the lower half of the Morenci blanket was further enriched during this time. Langton described the step faulting and tilted position of the enrichment blankets and the lateral enrichment of the Cambrian Coronado Quartzite. He also agreed with Moolick and Durek, that over 300 m (1,000 ft) of Pliocene to Recent uplift and deposition of the “Gila Conglomerate” resulted in further lowering the water table, partial destruction of chalcocite by oxidation and erosion, and rapid down-cutting that exposed hypogene sulfides in Metcalf.

North and Preece (1993) had the benefit of broader exposures of the deposit, additional drilling and mapping information in the district, and modern geochronology. They were the first to use mass balance calculations at Morenci to determine how much of
the deposit they could account for, and proposed that a larger volume of low-grade source rock was required than was preserved in the district. They proposed two generations of enrichment. The first generation was pre-volcanic and began around 56 Ma when the deposit was first exposed to oxygenated groundwaters and lasted until the onset of mid-Tertiary volcanism at about 32 Ma. They proposed that a widespread, 150-m (500 ft) thick, first generation enriched blanket was formed during this time with an average grade between 0.3% and 0.6% Cu. Their second generation of enrichment occurred after the mid-Tertiary volcanic cover was eroded causing significant lateral transport of copper and *in-situ* oxidation of low-pyrite portions of the blanket such as at Northwest Extension. They reported radiometric K-Ar age dates on two samples of alunite from Metcalf and Northwest Extension and concluded that the most significant enrichment occurred between 30 and 10 Ma. They also reported that enrichment was younger (7.2 Ma) at Northwest Extension than at Metcalf (9.9 Ma), and that some oxidation at Northwest Extension was even younger than the last movement along the Las Terrazas fault. Their emphasis on the importance of the post-volcanic enrichment period was a significant departure from the conclusions of the earlier studies.

Cook (1994) used K-Ar geochronology to study the geologic history of supergene enrichment in the porphyry deposits of southwestern North America and used Morenci for one of the study areas. He worked predominantly in the Shannon Mountain area in between Metcalf and Garfield. There he concluded that the supergene profile was zoned with respect to pre-mine topography and that the profile had been uplifted above the modern water table, conclusions that were consistent with Lindgren’s. Cook emphasized the
relative rates of erosion versus enrichment and recognized multiple stages of enrichment at Morenci. Based on supergene profiles and post-enrichment movement along the Copper Mountain fault, he concluded that there was “profound lateral migration” of copper solutions in the Morenci portion of the district, similar to what he had observed at Tyrone, New Mexico. Most importantly, Cook noted that the evidence for pre-Miocene enrichment at Morenci was largely circumstantial and concluded that there was “no evidence of pre-volcanic enrichment” at Morenci. He further concluded that the evidence for two stages of enrichment was compelling. Based on the K-Ar age dates mentioned above, he concluded that enrichment at Morenci lasted longer and was therefore more mature than at Metcalf. Cook’s assertion that supergene enrichment at Morenci was a post-volcanic phenomena, was a significant departure from the conclusions of earlier work.

Walker (1995) studied the structural evolution of Morenci district and provided an interpretation of the district in terms of the regional tectonic framework. Her conclusions about the supergene history at Morenci are essentially the same as North and Preece (1993). However, she provided some additional evidence for post-Laramide erosion of the Morenci uplift and north to northeast drainage and deposition of mineralized porphyry clasts in the Eocene Baca basin to the north. Walker also proposed that the mid-Tertiary structural evolution of the Clifton-Morenci area was related to the detachment faulting associated with the Pinaleno metamorphic core complex 25 km (15 mi) south of the district.

Recent work on the supergene environment at Morenci has shed new light on the scale, timing, and processes of oxidation and enrichment. Enders et al. (1998b) developed
a district-scale model of the supergene profile at Morenci and further developed the mass balance requirements based on pre-mine mineral profiles. Enders et al (1998a) conducted microbiological and geological studies of the Metcalf area. They were the first to report the actual occurrence of viable acidophilic iron oxidizing bacteria obtained from weathering outcrops of the Morenci porphyry copper deposit and propose a biochemical link with the classical geochemical aspects of supergene enrichment processes. Titley and Enders (1999) studied mineral profiles in the axial Chase Creek graben at Morenci. Based on that study, they proposed that some thick, stacked, enrichment profiles may be formed from the bottom-up, instead of the conventional top-down process, as a result of gradual rise of base level in down-dropped blocks during uplift and extension. Based on field relationships and on the stable isotope geochemistry of malachite and azurite from Melchiorre (1998) and Melchiorre et al. (1999), Melchiorre and Enders (in prep) are proposing environmental conditions associated with oxidation and formation of the Northwest Extension copper-oxide deposit at Morenci. The results of some of these recent studies of the supergene environment at Morenci are included in more detail in this dissertation.

**General Approach**

This study was part of a larger collaborative effort between the Geology Department at Phelps Dodge Morenci, Inc., Department of Geosciences at The University of Arizona, Arizona Geological Survey, Department of Biological Sciences at Northern Arizona University, and several other cooperating groups and individuals. The author has
worked continuously in the Morenci district since 1993, but the most intense phase of research was conducted from October 1997 through November 1999. The general approach was to examine the distribution, character and evolution of supergene mineralization in the district at different scales and from a variety of scientific perspectives. The results of these studies are reported in the five principle chapters of this dissertation.

The first chapter is focused on the regional scale. This work was conducted in collaboration with C.A. Ferguson of the Arizona Geological Survey and involved new geologic mapping and compilation of pre-existing mapping at 1:24,000 scale, and $^{40}\text{Ar}^{39}\text{Ar}$ geochronology of the volcanic rocks in the Clifton-Morenci area. This work resulted in a stratigraphic framework for the mid-Tertiary to Quaternary volcanic and sedimentary rocks in the Clifton-Morenci area, and a history of the erosion and unroofing of the Morenci block associated with the evolution of the Duncan basin and Transition Zone. The mapping is included as three plates in this dissertation. Plate 1 is the updated geologic map of the Clifton-Morenci area which covers the Coronado Mountain, Mitchell Peak, Copperplate Gulch, and Clifton 7-1/2' quadrangles centered on the Morenci district that was produced for the digital information series in GIS format through the Arizona Geological Survey (Ferguson and Enders, 2000; Ferguson et al., 2000). Plates 2 and 3 show the accompanying cross sections. Detailed units descriptions are included in Appendix A.

The second chapter contains a description of the geology of the Morenci porphyry copper deposit. It includes a review of existing published and unpublished data on the deposit for background on the basic geologic setting and controls of the mineralization.
This section is primarily focused on the hypogene mineralization and alteration that form the bulk mineralogy of the deposit that was subsequently eroded and chemically weathered in the supergene environment.

The third chapter is focused on the supergene mineralization in the district. It includes descriptions of the supergene zone from the district-scale down to local profiles that display characteristic features of specific deposits. This work is supported by detailed mineralogical profiles from selected core holes on three cross sections and polished section study of selected samples. Based on these profiles and a district-wide drill hole database, a simple mathematical model based on mass-balance criteria was created to de-enrich the deposit to look at district-scale enrichment characteristics, eroded thicknesses, and ultimately a pre-enrichment topographic surface.

The fourth chapter is focused on supergene processes and the role of microorganisms in leaching and enrichment. This work was conducted in collaboration with G. Southam of the Department of Biological Sciences at Northern Arizona University. It involved biological and geological studies of an actively weathering enrichment profile in the Metcalf pit. We sampled natural materials for acidophilic iron-oxidizing bacteria and sulfate-reducing bacteria from the outcrop, grew them in the lab, and estimated their abundance. Then we used TEM and EDS to image the bacteria and look at the associated authigenic minerals. This work was supplemented by hydrochemical, geochemical and mineralogical data from the sample sites. Based on this work, we propose a link between the geochemical and biochemical processes of leaching and enrichment in the supergene environment, and suggest conditions in which one or the other dominates.
The fifth chapter provides geochronological evidence of the age of supergene mineralization. The work involved $^{40}\text{Ar}/^{39}\text{Ar}$ age dating and geochemical analyses of a suite of alunite, jarosite, and cryptomelane samples from selected profiles in the deposit. The samples were dated at the New Mexico Geochronological Research Laboratory (NMGRL), in Socorro. The NMGRL reports for the work on the supergene samples and the volcanic rocks are included in Appendix B.

Finally, a synthesis is presented at the end of the dissertation that integrates the results of these studies into a proposed evolution of supergene enrichment in the Morenci district. The conclusions are brief and include suggested topics for future work.
Introduction

Work over the past several decades has indicated that mid to late-Tertiary erosion, tectonism, and associated volcanism and sedimentation played a profound role in the formation and preservation of supergene enrichment at Morenci and many other porphyry copper deposits in the region. However, geologists working outside the immediate mine area have given surprisingly little attention to the Tertiary stratigraphy and structure of the Clifton-Morenci area for nearly 100 years. Recent mapping has established a stratigraphic framework of the mid-Tertiary volcanic rocks in the Clifton-Morenci area and revealed the history of uplift and erosion of the Morenci block from the sedimentary record of the northern Duncan basin. This provides critical constraints on the evolution of supergene enrichment in the Morenci district. In addition, the mapping has provided important links to elements of the Tertiary and Quaternary evolution of the landscape of the Transition Zone in this region of Arizona.

Pre-existing Geologic Mapping

There are numerous published maps at various scales in the surrounding areas of southeastern Arizona and southwestern New Mexico (Figure 7). At the smallest scale, maps by Reynolds (1988), Wilson and Moore (1958), and Drewes et al. (1985) cover too large of an area and are of limited value. The most helpful are the 1:48,000 and 1:24,000 scale maps of the adjoining areas. Three publications in particular are Ratte and Brooks’
(1995) map of the Big Lue Quadrangle to the east, Richter et al.’s (1983) map of the Guthrie Quadrangle to the southwest, and Cunningham’s (1981) map of the San Francisco River canyon immediately to the east of the district. Other published regional-scale maps in the area include Hedlund (1993), Morrison (1965), Ratte (1982), Ratte and Brooks (1995), Ratte and Hedlund (1981), Richter and Lawrence (1981), and Wahl (1980). Unpublished regional-scale maps include Lepley (1993), Phelps Dodge (1993), and West (1993, 1996). In addition to that of Preece (1984), there are numerous other maps of smaller portions of the immediate mine area such as Pawlowski et al. (1997), and of a few adjacent areas including Dames and Moore (1997) and More (1995) that are available in the Phelps Dodge Morenci, Inc. files. Schroeder (1996) and Melchiorre (1994) also contributed maps of the Enebro Mountain area north of the district to the Arizona Geological Survey. Four students from Cambridge University completed 1:10,000 scale geologic maps along Highway 191 just north of the Morenci district as part of their summer field course work, and these illustrate local detail (Chillingworth, 1999; James, 1999; Lock 1999; Warren, 1999).

Numerous geologists have studied the Cenozoic stratigraphy, tectonics, and depositional setting of southeastern Arizona and southwestern New Mexico; these studies provide a setting for the Clifton-Morenci area. In Arizona, Scarborough (1989) discussed Cenozoic erosion and sedimentation, Spencer and Reynolds (1989) developed the mid-Tertiary tectonic setting, and Menges and McFadden (1981) and Menges and Pearthree (1989) described the impact of late Cenozoic tectonism on the regional landscape evolution. McIntosh et al. (1992) provided a time-stratigraphic framework for the Eocene-
Datil volcanic field in New Mexico, Cather et al. (1994) developed the Tertiary stratigraphy and nomenclature for the region, and Marvin et al. (1987) listed 212 isotopic ages of post-Paleocene igneous rocks within and adjacent to the Clifton 1° x 2° quadrangle. More recently, Smith and Mack (1999) reported on the depositional environment of the Cenozoic Gila Conglomerate approximately 50-km (30 mi) to the south near Duncan, Arizona and Virden, New Mexico. The Tertiary volcanic stratigraphy of regions east of the Clifton-Morenci area was investigated in some detail (Ratte and Brooks, 1995; Ratte and Hedlund, 1981; Ratte, 1982; Hedlund, 1993; Morrison, 1965; Wahl, 1980). However, little is known about how these strata correlate with rocks to the west of the Clifton-Morenci area.

Landscape Evolution and Supergene Enrichment

The link between tectonic history, landscape evolution and supergene enrichment of porphyry copper deposits is well documented at Morenci and many other districts. Lindgren (1905a) believed that the Morenci deposit was enriched during “Gila Conglomerate time”. Later, Moolick and Durek (1966), Langton (1973), North and Preece (1993), Cook (1994), and Walker (1995) concluded that leaching and enrichment at Morenci occurred during at least two periods. These processes began as soon as the mineralization was exposed to oxygenated groundwater and ended with the onset of mid-Tertiary volcanic cover, and resumed again when mid-late Tertiary extension re-exposed the deposit.
Similar histories of cyclical enrichment have been documented in other porphyry copper districts in southwestern North America. This includes the early work at San Manuel, Arizona (Schwartz, 1953), Ajo (Gilluly, 1946), Bisbee, Arizona (Bryant and Metz, 1966), and Tyrone, New Mexico (Paige, 1922), as well as at Butte, Montana and Bingham Canyon, Utah (Atwood, 1916). Later, Livingston et al. (1968) used K-Ar geochronology to document the emplacement, enrichment, and preservation of 16 porphyry copper deposits in Arizona. They concluded that:

“The Laramide porphyry copper deposits appear to have been developed during a period of volcano-plutonic activity followed by a period of extensive erosion and supergene enrichment during which some or all of the contemporaneous volcanic rocks were eroded away. These deposits were then preserved from complete erosion by burial beneath widespread sedimentary and/or volcanic rocks of mid-Tertiary age. As the modern (post-Miocene) stream regime cut into the tectonically deformed pre-mid-Tertiary erosion surface, these deposits were again exposed and eroded and made accessible for exploitation.”

Lowell (1974) further proposed that the level of erosion and timing of differential structural uplift or drainage base level controlled the evolution of supergene enrichment. Cook (1994) used K-Ar geochronology to date alunite, jarosite, and illite samples from 15 porphyry copper deposits in the region and further linked three stages of weathering to the tectonic evolution of the region. Moreover, Cook (1994) linked the K-Ar dates to the Cenozoic cycles of erosion and sedimentation of Scarborough (1989).

Similar studies of supergene copper enrichment have been conducted in the southern Cordillera porphyry copper province of Chile and Peru. Detailed investigations by Clark et al. (1967), Mortimer (1973), and Mortimer et al. (1977) of Tertiary deposits in northern Chile revealed that supergene enrichment was empirically related to the intervals
between sedimentation during the development of regionally extensive erosional
landforms. Mortimer (1973) related the absence of supergene enrichment beneath volcanic
cover, and the presence of enrichment in areas that had been subsequently dissected to
cycles of volcanism, erosion, and sedimentation in the Cenozoic Era. Alpers and Brimhall
(1988) and Sillitoe and McKee (1996) related ages and cycles of supergene enrichment at
La Escondida and several other Chilean deposits to the Cenozoic evolution of tectonics,
paleotopography, erosion rates, and climatic desiccation based on K-Ar dating of
supergene alunite. Clark et al. (1990) used regional geologic-geomorphologic
reconstruction techniques to relate the physiographic development of the pre-Cordillera of
southern Peru to the evolution of supergene enrichment of Laramide copper deposits at
Cuajone, Quellaveco, and Toquepala.

Methods

This study was a collaborative effort between Phelps Dodge Morenci, Inc., the
Arizona Geological Survey, and the Department of Geosciences at the University of
Arizona. The work was conducted in conjunction with other geological studies of the
supergene environment at Morenci, and primarily involved geologic mapping and related
studies of portions of four 7.5’ quadrangles (Plate 1) over a five-month period from
August-December 1998. The purpose of the mapping was to establish a stratigraphic
framework of the mid-Tertiary volcanic rocks of the surrounding mountains and the
sedimentary rocks of the adjacent basins. This required re-mapping, field checking, and
synthesis of existing mapping in the district (Lindgren, 1905b; Preece, 1984; Cunningham,
1981) and in adjacent areas (Richter et al., 1983; Ratte and Brooks, 1995) into a new geologic map. Mapping was done at a reconnaissance-scale and at a hand-specimen and outcrop level, without the benefit of detailed petrographic or geochemical studies. Some supplemental petrographic and geochemical studies were completed on a few of the Precambrian and Laramide-age intrusive rocks to augment existing databases (Lee, 1994; Walker, 1995) and aid in interpretation. Mapping was done on both orthophoto and topographic base maps that were linked to the local Morenci Mine and state UTM grids. Processed images were prepared by merging the color orthophoto image with various combinations of Landsat TM bands to produce images that highlighted bedrock lithology and structure (Bands 7,4,1), and alteration based on supervised classification from Bands 1,3,5 and 7 (Marlow, 1999). This work was supplemented with 15 new $^{40}$Ar/$^{39}$Ar ages of selected volcanic rocks in the area, dated at the New Mexico Geochronological Research Laboratory in Socorro (Peters, 1999a,b; Peters and McIntosh, 1999) (Appendix B).

Although no detailed measured sections were created at this level of study, selected drill holes were used to assist in stratigraphic reconstruction, cross section preparation, and isopach/structure contouring (Dames and Moore, 1997). Estimates of clast abundance in the sedimentary rocks were used to record the relative proportion of the various rocks that were being shed into the adjacent basins. In addition, gravity and aeromagnetic data were used to interpret the overall structure and depth to bedrock of the Duncan basin (Enders, 1996; West, 1996). The results of this work are reported in this section. Previously available radiometric age dates for some of the Laramide intrusive rocks in the Morenci
district are included in Table 3. $^{40}$Ar/$^{39}$Ar age dates for some of the mid-Tertiary volcanic rocks in the Clifton-Morenci area from this study and are included in Table 4.

**Regional Setting**

The Transition Zone is a broad physiographic province in between the relatively structurally intact Colorado Plateau and the highly extended terrain of the southern Basin and Range province (Figure 1). The Transition Zone is a region of rugged, relatively high-elevation terrain (1,500 to 2000 m, 4,900 to 6,500 ft) above a thinned crust (from 40 to 22 km, 24 to 36 mi), but without significant expression of extension at the surface (Leighty, 1997). Its northern boundary in Arizona is along the Mogollon Rim, a physiographic break defined by the southward termination of north-dipping Permian strata (Pierce et al., 1979). Its southern boundary in Arizona is structurally but less spectacularly defined. This boundary is located in those areas where low-angle normal faulting associated with mid-Tertiary extension dislocates the terrain into a series of isolated basins and ranges separated from the relatively-intact terrain of the Transition Zone (Spencer and Reynolds, 1989). Walker (1995) postulated that structural deformation and low-angle detachment faulting of the mid-Tertiary metamorphic core complex in the Pinaleno – Santa Teresa Mountains 25 km (15 mi) southwest of Morenci was linked to the northwest-striking faults and gentle southwest dips of Paleozoic and Cretaceous strata in the region. The eastern margin of the Transition Zone is covered by volcanic rocks of the Mogollon–Datil volcanic field and marks the western extent of Rio Grande-related rifting (Walker, 1995). This structural zone (Figure 8) is a 40 to 50 km (24 to 30 mi) wide, complex system of 040° to 030° striking grabens of the Morenci-Reserve fault zone (Ratte, 1989). Walker (1995)
related the northeast-striking faults in the Clifton-Morenci area to mid-Tertiary extension along this southeastern margin of the Colorado Plateau and Transition Zone.

The Morenci structural block and the Duncan basin in the Clifton-Morenci area are located at the intersection of all of these regionally important geologic features. The Morenci structural block appears as a roughly triangular window of Precambrian to early Tertiary rocks that is bounded by two major normal faults. The northwest-striking Eagle Creek fault on the west represents the western margin of a tilt block associated with the Pinaleno-Santa Teresa detachment and metamorphic core complex (Walker, 1995). The northeast-striking San Francisco fault on the east represents the western margin of a half-graben in the Morenci-Reserve fault zone (Walker, 1995). These faults juxtapose older rocks of the Morenci block with Miocene to Recent sedimentary and volcaniclastic rocks of the basin fill sequences in the Eagle Creek and San Francisco arms of the northern Duncan basin (Figure 8). At the southern edge of the Morenci block, the Eagle Creek fault appears to continue southeastward from the intersection of the San Francisco fault, perhaps as the buried Ward Canyon fault, while the San Francisco fault appears to die out to the southwest. The Clifton-Morenci area is also situated at the intersection of the Oligocene-age Mogollon-Datil volcanic field to the east and the Miocene-age Peloncillo volcanic field to the south. The Morenci district is surrounded by rhyolite, andesite and basalt from these fields to the north in the Malpais-Enebro Mountain area, to the west in the Black Hills and Turtle Mountain area of the northern Peloncillo Mountains, and to the east and southeast in the Big Lue and Summit Mountains.
Morenci Block

The Morenci block contains Precambrian igneous rocks, Paleozoic and Mesozoic sedimentary rocks, and a suite of Laramide-age intrusive rocks (Plate 1). These rocks have been further dissected and dislocated by a network of east-west-, northwest-, northeast-, and north-south-striking faults. These rocks are the hosts for mineralization and hydrothermal alteration associated with the Morenci porphyry copper deposit (Lindgren, 1905a; Moolick and Durek, 1966; Langton, 1973; Preece and Menzer, 1992).

Stratigraphy: Lindgren (1905a,b) described the stratigraphy of the district in detail and established the local nomenclature currently used (Figure 9). The Precambrian basement in the area consists dominantly of granodiorite and granite possibly related to the widespread suite of Middle Proterozoic granites found throughout the southwest. Because these rocks have not been dated in the Clifton-Morenci area, however, it is possible that some or all of these rocks are Early Proterozoic in age. The Proterozoic plutonic rocks intrude a succession of quartz-sericite schist and meta-quartzite in the Pinal Point area about 13 km (8 mi) to the north of the mine area. Approximately 325 to 420 m (100 to 128 ft) of Paleozoic marine and marginal marine sedimentary rocks overlie the basement. These units include the Cambrian Coronado Quartzite, Ordovician Longfellow Formation, Devonian Morenci Formation, and Mississippian Modoc Formation. North of the Garfield fault in the northern portions of the map area, the Modoc Formation is incorporated into the thicker Mississippian to Pennsylvanian Tule Springs Formation. Over 779 m (2,555 ft) of sandstone and shale of the Cretaceous Pinkard Formation disconformably overlie the Paleozoic section south of the Quartzite fault in the southern portion of the block. In
places, mudstone of the basal Pinkard Formation partially fills karst features developed in the underlying limestone of the Modoc Formation. A series of Laramide-age porphyries intruded Precambrian through Cretaceous rocks in the Paleocene to early Eocene epochs (Table 3). Laramide intrusive activity may have been associated with a coeval overlying andesitic stratovolcano (North and Preece, 1993; Preece, Stegen and Weiskopf, 1993), but no physical evidence of those rocks has yet been discovered. Over 640 m (2,100 ft) of Miocene basaltic lava overlain by rhyolite tuff and lava flows unconformably overlie older rocks in the northern portion of the block in the Enebro Mountain and Malpais Mountain areas. Ferguson and Enders (2000) and Ferguson et al. (2000) provide detailed descriptions of the rocks of the Morenci block (Appendix A).

**Structure:** The Morenci block has been broken into several structural domains as shown in Figure 10 and in Plate 1. Four domains have been created by three important normal faults. The down-to-the-south Quartzite and Coronado faults offset Paleozoic rocks against Proterozoic granite in the southern and central portions of the district. The down-to-the-north Garfield fault places mid-Tertiary volcanic rocks and upper Paleozoic rocks against Proterozoic granite and lower Paleozoic rocks in the northern portions of the district. The Morenci block is further dislocated by a series of east-west-striking, northwest-striking, northeast-striking faults, and north-south striking normal faults many of which were Laramide-age structures that were re-activated during mid-Tertiary, and Basin and Range deformation (Walker, 1995). These include the southwest-dipping Kingbolt and east-dipping Chase Creek faults in the Chase Creek drainage, the northeast-dipping Copper Mountain and west-dipping War Eagle faults to the west and east, respectively. This
system of faults has created an axial graben in the center of the Morenci district that is adjacent to the Pinal-Eagle Creek horst on the west and the San Francisco-Malpais horst on the east.

**Mineralization:** The Morenci district hosts a porphyry copper deposit that was formed by magmatic-hydrothermal processes about 55 million years ago (Table 3) (Griffin, Ring and Lowery, 1993; McCandless and Ruiz, 1993). Widespread hypogene mineralization as pyrite+chalcopyrite +/- sphalerite was deposited in a stockwork of veins and fractures in Proterozoic granite, Paleozoic sedimentary rocks, and Laramide-age felsic intrusive rocks over a 20-km$^2$ (7.7 mi$^2$) area. The resulting stockwork of veins and veinlets has a fracture density ranging from about 0.10 to 1.0 per cm (length/area). Hypogene mineralization was accompanied by pervasive quartz-sericite-pyrite alteration that resulted in a deposit with average contents of 3 wt.% pyrite and 0.16% copper as chalcopyrite. Supergene enrichment at Morenci was formed by the coupled processes of erosion and chemical weathering during at least two periods of enrichment. These processes began about 55 Ma and ended with the onset of mid-Tertiary volcanic cover (approximately 30 Ma), and resumed again after 16 Ma when mid-late Tertiary extension re-exposed the deposit (Moolick and Durek, 1966; Langton, 1973; North and Preece, 1993; Cook, 1994; Walker, 1995; this study). A detailed description of the Morenci porphyry copper deposit is included in the following chapter.
Duncan Basin

The Duncan basin borders the Morenci block to the southwest, south, and southeast (Figure 8). The sedimentary rocks of the Duncan basin record the Cenozoic history of uplift and erosion of the Morenci and adjacent blocks. The basin strikes north-northwest and is about 60 km (37 mi) long, and the valley ranges from 8 km (4.9 mi) to over 14 km (8.5 mi) wide covering a 700-km² (270 mi²) area (Figure 11). It is bordered on the northeast by the Big Lue Mountains, on the east by the Summit (Steeple Rock) Mountains, on the south by Lordsburg Mesa, and on the west and northwest by the Peloncillo Mountains and Black Hills. The Gila River enters the basin from the southeast and drains the valley to the northwest. The Duncan basin terminates to the northwest about one mile upstream from the confluence of the Gila and San Francisco Rivers where the volcanic rocks of the Peloncillo Mountains are continuously exposed across the valley. The Eagle Creek sub-basin is a graben that extends for over 16 km (9.8 mi) to the northwest of the confluence and separates the Morenci block from the Turtle Mountains of the northern Peloncillo range on the west. The San Francisco sub-basin is a half-graben that extends for over 20 km (12 mi) northeast of Clifton and separates the Morenci block from the Big Lue range on the east. The Duncan basin north of York, Arizona, the Eagle Creek and San Francisco sub-basins, and Bonita Creek and the Gila Box have been deeply incised by their current drainages (Figure 3). They contain inner gorges that range from 200 m (650 ft) in depth in the upper reaches of the canyons to over 315 meters (1,030 ft) in the lower stretches (Plates 1, 2, and 3).
Mid-Tertiary sedimentary and volcanic rocks surround the Morenci block and fill the adjacent Duncan basin. The volcanic rocks range in age from late Oligocene to early-Miocene (~34 to 18.2 Ma) and in composition from basalt to rhyolite. The sedimentary rocks include mid-Miocene to Recent conglomerate, sandstone, and siltstone of the Gila Group (or Gila Assemblage of Scarborough, 1989) and the overlying upper basin fill. Stratigraphic columns for the Eagle Creek, San Francisco River, and Coronado Trail sections are shown in Figures 12, 13, and 14. Detailed unit descriptions are included in Appendix A from Ferguson and Enders (2000).

**Mid-Tertiary volcanic rocks:** Mid-Tertiary volcanic activity in the Clifton-Morenci area spanned a 16 million-year period that began in the early-Oligocene with eruption of the Clifton Tuff at ~34 Ma and ended in the early-Miocene with eruption of a bi-modal sequence of tuffs and basalts. The lower conglomerate is correlative to the Whitetail Assemblage of Scarborough (1989) and represents the last significant period of erosion and sedimentation prior to the main pulse of volcanism. Beginning at about 30 Ma, volcanic rocks began to cover the Clifton-Morenci area. Evidence for this includes an andesite dike at Metcalf dated at 30 Ma (Cook, 1994) and an andesite flow at Coronado (this study), as well as the voluminous andesitic lavas in the adjacent blocks (Table 4). Andesitic volcanism occurred from 30 Ma to about 23 Ma with peaks around 24-25 Ma and 27-28 Ma. Rhyolitic volcanism periodically erupted during this time and included the Davis Canyon Tuff (29 Ma), Bloodgood Canyon Tuff (28 Ma), and a succession of younger tuffs from 24.5 Ma to 18.2 Ma (Table 4). Volcaniclastic and tuff layers (Tbs and Tvs) represent short erosional and sedimentation breaks during basaltic andesite volcanism.
during this time. Basin subsidence began during the waning stages of volcanism. Rhyolite lava and tuff, and basalt are interbedded with sedimentary rocks of the Gila Group, as well as with basaltic conglomerate (Tcb) and conglomerate of Bonita Creek (Tbck). Prior to erosion, the mid-Tertiary volcanic rocks in the Clifton-Morenci area ranged from about 640 m thick in the northern areas to over 950 m thick in the southern areas of the Morenci block (this study).

Mid-Tertiary to Recent sedimentary rocks: The Gila Group is a complex succession of Pleistocene, Pliocene, and Miocene-aged variably indurated, post-volcanic conglomerate, sandstone and siltstone that are derived from the adjacent bedrock blocks and fill closed basins within the present physiographic boundaries. In the Morenci area, this group consists of several informal subdivisions defined largely on clast content, and to a lesser extent, on lithification and bedding. The nomenclature follows Richter et al. (1983) from the Guthrie and Safford Quadrangles to the south and southwest. The basal, mid-Miocene to Pliocene conglomerate of Midnight Canyon (Tgmc) contains only basalt, andesite and rhyolite clasts, and outcrops extensively in the Eagle Creek and San Francisco River areas. The Pliocene unit of Buzzard Roost Canyon (Tgbr) conformably overlies Tgmc. This unit contains progressively greater amounts (~5% to 30%) of Precambrian, Paleozoic, and Laramide-age clasts and locally up to 5% of mineralized clasts towards the top of the section. The Pliocene to Pleistocene unit of Smugglers Canyon (QTgs) consists of unlithified to semi-lithified interbedded lenses of silt, sand, gravel and boulders that were derived from the immediately adjacent bedrock. In places, younger alluvial deposits (QTao, Qa) occur along ridge crests and in the adjacent canyons. The sedimentary section
is approximately 625 m (2,000 ft) thick adjacent to the Eagle Creek and San Francisco faults, and over 1-km (3,000 ft) thick in the adjacent Duncan basin. Erosion and base level drop during the Pleistocene accompanied 200 m (650 ft) to over 300 m (980 ft) of down cutting of the Gila River and formed the incised canyons of the surrounding terrain. Detailed stratigraphic thicknesses from outcrop and the Morenci drill hole database are included in Appendix C from Ferguson et al. (2000). Relative clast abundance of the sedimentary units is further discussed in a following section.

**Volcanic Geochronology**

Fifteen new $^{40}\text{Ar} / ^{39}\text{Ar}$ ages have been determined for selected volcanic rocks in the Clifton-Morenci and adjoining areas as part of this study. The samples represent a reconnaissance of the volcanic stratigraphy in the Morenci area along with a limited suite of samples from adjoining areas, mostly for calibration between the various laboratories and techniques, e.g. (Marvin et al., 1987; McIntosh et al., 1992; Ratte and Brooks, 1995; Richter et al., 1983). The work was done to help correlate strata in the Clifton-Morenci area with rocks to the east and west. The samples were dated at the New Mexico Geochronological Research Laboratory (NMGRL) in Socorro (Peters, 1999a, b; Peters and McIntosh, 1999). The NMGRL reports are included in Appendix B, and their methods and results are summarized below. Sample locations are shown on Plate 1, and the results are included in Table 4 and in the Unit Descriptions in Appendix A.
Materials and Methods

**Basalts:** Eight samples of andesite and basalt were selected for whole rock \(^{40}\text{Ar}/^{39}\text{Ar}\) dating. The samples were selected from a larger set of 20 samples (Table 5) that were evaluated for their suitability for dating by microprobe analysis at the New Mexico Bureau of Mines and Mineral Resources (Dunbar, pers. commun.). The evaluation was based on: 1) the presence of potassic feldspar suitable for Ar analysis as a groundmass phase or as rims on plagioclase, 2) the presence of glassy groundmass that may contain excess Ar, and 3) the presence of secondary alteration phases that may adversely affect the Ar analysis. The analyses were performed using a Cameca SX-100 electron microprobe with 3 wavelength-dispersive spectrometers. An accelerating voltage of 15 kV and a 20 nA beam current were used (Dunbar, pers. commun.). Based on the microprobe analyses, three samples were judged very good, ten were judged good, four were judged moderate, and 3 were judged poor prospects for dating (Table 5). Groundmass concentrates from eight of the samples were subsequently analyzed by the furnace incremental heating method. Abbreviated methods for the sample preparation and analysis from Peters and McIntosh (1999) are included in Appendix B.

**Rhyolites:** Nineteen samples of rhyolite lava and tuff were submitted for sanidine laser-fusion, single crystal \(^{40}\text{Ar}/^{39}\text{Ar}\) dating. Dateable sanidine was found in only seven of these samples either from groundmass or pumice. Abbreviated methods for the dateable samples from Peters (1999a,b) are included in Appendix B.
Results

**Basalts:** NMGL’s preferred ages of these samples are shown in Table 4 and illustrated on the probability distribution diagram in Figure 15, from Peters (1999a) in Appendix B. Four of the analyzed samples (F8-266, F8-275, F8-276, F8-286) yielded fairly well behaved age spectra and the plateau ages were recommended as the preferred age. Although sample #F8-273 yielded a well-behaved age spectra, isochron analysis revealed a $^{40}\text{Ar}/^{39}\text{Ar}$ ratio above the atmospheric ratio and the isochron age was recommended at the preferred age. Samples F8-269, F8-301, and F8-316 yielded disturbed age spectra indicative of $^{39}\text{Ar}$ recoil during irradiation and the integrated ages were recommended at the preferred ages.

**Rhyolites:** The NMGL results for the sanidine samples are listed in Table 4 and displayed separately on a suite of probability distribution diagrams shown in Peters (1999b) in Appendix B. The ages for all of the samples are summarized on the probability distribution diagram in Figure 16. The weighted mean age of all the crystals in all samples except F8-288 was reported as the preferred age of eruption. The preferred age for the eruption of F8-288 was given as the pumice sanidine rather than the matrix sanidine because the pumice sanidine had a smaller error.

Interpretation

The $^{40}\text{Ar}/^{39}\text{Ar}$ results from the 15 samples (Table 4) in this study complement the 25 published K-Ar dates (Table 6) from other volcanic rocks in the Clifton-Morenci region. Overall, the dates span a 16 million-year period of volcanism in the Clifton-Morenci area.
This period began in the early-Oligocene with eruption of the Clifton Tuff (Tc) at ~34 Ma and ended in the early-Miocene with eruption of a bi-modal sequence of rhyolite (Te) and basaltic andesite (Tb) that are interlayered with conglomerates of the lower Gila Group (Tbck, Tgmc).

Based on the mapping and geochronology completed in this study, nine sequences of Oligocene through Miocene volcanic and sedimentary rocks have been recognized in the Morenci area. The sequences are defined mostly on the basis of age, and as such, dramatic changes in thickness and composition across the map area are possible. These sequences are summarized in Table 7, and shown on a schematic stratigraphic column and in two schematic cross sections in Figures 17 and 18, respectively. Sample locations are shown on Plate 1, and the sequences are described in detail below.

Sequence 1 (34 to 28 Ma) Older andesitic lava flows: The 34 Ma Clifton Tuff and the 28 Ma Bloodgood Canyon Tuff define the lower and upper boundaries of this sequence. Both of these regional ash-flow tuff sheets were derived from silicic cauldron complexes in the Mogollon-Datil volcanic field of southwestern New Mexico. The western pinch-out of these units is just to the west of the San Francisco River. The principal volcanic unit emplaced during this time period is a thick sequence (up to 200 m, 650 ft) of basaltic andesite lava. This lava sequence is at the base of a very thick (up to 1 km, 3,280 ft thick) pile of similar mafic lavas that are present throughout the area. The Bloodgood Canyon Tuff defines the top of this sequence and has a limited aerial extent, and the area directly north and east of Clifton is the only location where lavas of this age are definitely known. Other units that can be assigned to this sequence include a thin conglomerate unit and a
crystal-poor, welded ash-flow tuff that is present only in the extreme northeastern part of the map area. This crystal-poor tuff is tentatively correlated with the 29 Ma Davis Canyon Tuff (Ratte and Brooks, 1995). This tuff is preserved in the footwall of San Francisco fault north of Sardine Creek where it is separated from the underlying Clifton Tuff by a non-volcaniclastic conglomerate. This suggests that the onset of andesitic lava volcanism of Sequence 1 did not commence until after about 30 Ma. This is supported by the oldest dates for basaltic lava in the Morenci area of 30.0 Ma for a dike at Metcalf (Cook, 1994) and 28.52 Ma for lava from TV Hill, an isolated cinder cone that overlies Paleozoic rocks in the Coronado area of the Morenci mine.

**Sequence 2 (28 to 22.5 Ma) Younger andesitic lava flows:** This sequence represents the main pulse of basaltic volcanism in the Clifton-Morenci area. It produced a pile of mafic lava up to 1 km (3,280 ft) thick that blanketed the entire area. The thinnest accumulation of lava was probably directly above the mineralized zone of the Morenci district. Lavas from this sequence have been dated as old as 27.73 Ma, and as young as 22.33 Ma. In the Clifton-Morenci area, Sequence 2 consists of monotonous, amalgamated lava flows of basaltic andesite to andesite composition. To the east, west and south of the Clifton-Morenci area interbedded felsic lavas and tuffs are present that partition the mafic lavas of Sequence 2 into different map units. To the east, Ratte and Brooks (1995) divided a sequence correlative to Sequence 2 into three units; the 27-28 Ma volcanic sequence in the Big Lue Mountains (including map units Ta, Tacc, Tac, and Tbl), the 24-26 Ma Bearwallow Mountain andesite (including map units Tba, Tbap, Tbam, Tbas, Tbac, Tbav, Tbab, and Tabi), and a 17-20 Ma Miocene basalt unit (including map units Tb, Tbs, and
Tbcc). Along the eastern edge of the study area, Sequence 2 includes at least one prominent flow break defined by interbedded volcaniclastic rocks, but it is not certain how these breaks correlate with the division(s) mapped by Ratte and Brooks (1995) to the east. It is also not clear how well the age assignments of Ratte and Brooks’ (1995) can be applied to the sequence just to the east of San Francisco River. For example, Ratte and Brooks’ (1995) 17-20 Ma Miocene basalt unit can be traced into this study area without obvious disruption by faults or changes in stratigraphy down to the upper San Francisco River where it is intruded by a 22.25 Ma rhyolite lava dome. The contact between the two older mafic units, described by Ratte and Brooks (1995), was also traced into the eastern part of the map area just north of Limestone Gulch. This contact is correlated with a prominent flow break in Ash Spring Canyon that overlaps a major east-side-down fault. Lavas from above and below this contact were dated for this study and gave essentially the same age; 27.62 and 27.73 Ma respectively.

To the south of the map area in the northern Peloncillo Mountains, Richter et al. (1983) subdivide mafic lavas correlative to Sequence 2 into two main sequences of younger and older andesite flows, all assigned to the andesite of Guthrie Peak-Turtle Mountain. The younger sequence is referred to as upper andesite flows (including map units Tau, Tad, Tac, and Tpaf) throughout their map area, but the older sequence is divided into two units. In the northwest, the older andesite is referred to as the andesite of Gila River (Ta), and to the south it is referred to as lower andesite flows (Tal). In both areas, thin pyroclastic flows (map units Ttg and Tab) mark the contact between the older andesite and the upper andesite. To the south, Richter et al. (1983) show a thick succession of
felsic lavas that is interpreted to be interbedded between the upper and lower andesites, but on the map there are no exposures of upper andesite that clearly overlap the felsic lavas. Instead, the upper andesite is shown overlapping the felsic lavas along a steeply north-facing buttress unconformity just to the north of US Highway 191 at the crest of the range (see their cross-section A-A’). Field examination subsequently indicated that the contact is a buttress unconformity rather than a fault, and the felsic lavas are younger than Richter et al.’s (1983) upper andesite (Tau) unit. This interpretation is supported by geochronology data that indicates the 22.41 Ma felsic lavas are younger than the youngest andesites of the Tau unit, dated in this study at 24.74 Ma. Richter et al. (1983) published two dates from their upper andesite unit; 23.7 Ma from a flow at the top of the sequence along lower Gila River, and 19.4 Ma for a lava near the top of the sequence along the southern margin of the outcrop area. The 19.4 Ma date is probably too young because it comes from a flow that directly overlies a sanidine-bearing, pumice-rich nonwelded tuff that dated 22.25 Ma in this study. Richter et al. (1983) also published three dates from their lower andesite sequence; 22.6, 22.2, and 21.8 Ma. These dates are also puzzling, because these lavas clearly underlie andesitic lavas dated at 24.7 Ma in this study, and Richter et al. (1983) dated at 23.7 Ma. The lower andesites also clearly underlie sanidine-bearing rhyolitic lavas that have been dated at 23.1 (Richter et al., 1983) and at 22.4 Ma in this study. Richter et al’s (1983) ages of their lower andesites may have been reset or reflect the age of younger, altered potassium-bearing phases in the samples.

To the west of the Clifton-Morenci area, Sequence 2 is also correlated with the andesite of Guthrie Peak-Turtle Mountain (Houser et al., 1985). This succession includes
upper and lower andesite lava units (Tau and Tal map units respectively) which occur
above and below a felsic lava succession in the Gila Mountains directly northeast of
Safford (Houser et al., 1985). The interbedded felsic volcanic rocks of the Gila Mountains
range in age from 26.5 to 24.5 Ma (Houser et al., 1985) and can be traced eastward onto
the western slopes of Turtle Mountain, just to the northwest of the Gila Box. The younger
andesitic rocks also include map units Taut, Taup, and Tad. Nonwelded tuff, dated at 24.5
Ma from the top of Sequence 2 in lower Eagle Creek near the Gila Box, and a layer of
undated nonwelded tuff mapped as Ttg by Richter et al. (1983) in the Gila Box, are
interpreted to be the eastern-most preserved pyroclastic units of the Gila Mountains silicic
volcanic center.

Sequence 3 (26.5 to 24.5 Ma) Gila Mountains silicic volcanic center: Sequence 3
is enclosed within Sequence 2. Its eruptive products are recognized only in the extreme
western part of the Clifton-Morenci area. Sequence 3 consists of a suite of felsic lavas and
associated nonwelded tuff with vents in the southeastern Gila Mountains. Houser et al.
(1985) dated these lavas between 26.5 and 24.5 Ma. The felsic volcanic rocks occur
between the upper and lower divisions of the andesite of Guthrie Peak-Turtle Mountain
(Houser et al., 1985). The felsic lavas are divided into a number of map units: Trp, Tr,
Tbdp, Tbhd, Tbd, Tbud, Tbuf, Tblf, Tbp, Tbl, Tba, Tbp, Tbrd, Tbb, Tbcd, and Tbc
(Houser et al. 1985). Richter et al. (1983) also mapped the eastern edge of this lava field
northwest of the Gila Box as Tdf. In the Gila Box area, a thin nonwelded tuff (Ttg) is
present in-between the upper andesite flows (Tau) and andesite of Gila River (Ta) of
Richter et al. (1983). This Ttg unit and another unmapped nonwelded tuff higher in the
section near the mouth of Eagle Creek are interpreted to be the easterly pyroclastic fringe of the silicic volcanic center in the Gila Mountains. The upper, unmapped nonwelded tuff was dated at 24.5 Ma (this report), but the lower one (the Ttg unit of Richter et al., 1983) has not been dated.

**Sequence 4 (23 to 21 Ma) Enebro Mountain Formation:** In the Clifton-Morenci area, the Enebro Mountain Formation (proposed in this report) is represented by an east-west-striking swarm of rhyolite lava domes that extends from Enebro Mountain east across the Chesser Gulch area to the San Francisco River. Schroeder (1996) dated a lava flow at Enebro Mountain at 21.7 Ma, and one of the lava domes along San Francisco River was dated at 22.25 Ma as part of this study. Marvin et al. (1987) reported dates of 20.6 and 20.9 Ma and Ratte and Brooks (1995) reported dates of 21.3 and 21.8 Ma from the unit. The Enebro Mountain lava field also produced voluminous nonwelded tuffs that blanketed much of the Clifton–Morenci area. Throughout the area, these tuffs mark the contact between the extensive andesitic lava flows of Sequence 2 and the onset of Sequence 5, the volcaniclastic sedimentary rocks of the conglomerate of Bonita Creek. The Enebro Mountain Formation of the Clifton-Morenci area is correlated with an extensive field of felsic lavas in the northern Peloncillo Mountains (Richter et al, 1983) including map units Tabr, Tab, Tar, Tapd, Tapi, Tap, Tard, Tda, Tttrb, and Tttrd. Richter et al. (1983) reported dates for two lavas from this succession in the northern Peloncillo Mountains at 23.1 and 21.2 Ma. The oldest of these lavas (unit Tabr) was re-sampled in this study and gave an age of 22.4 Ma.
Sequence 5 (21 to 18 Ma) Conglomerate of Bonita Creek: This sequence is characterized by volcaniclastic conglomerate with clasts of dominantly basaltic lava, and less abundant rhyolitic pumice and nonwelded tuff. The sequence also includes rare nonwelded tuff layers in the lower Gila Box area, one of which has been dated at 19.1 Ma (map unit Ttt) by Richter et al. (1983) along lower Gila River. Note that there are other tuffs interbedded with the upper andesites (Tau) farther south that were also mapped as Ttt by Richter et al. (1983), but these are significantly older, correlating with the Enebro Mountain Formation. In this study, the top of the conglomerate of Bonita Creek in the Gila Box area is defined as the top of a prominent nonwelded tuff dated at 18.2 Ma along lower Eagle Creek, but this is the only place where a dated volcanic unit is present along the contact. The top of the unit is probably time-transgressive. At the southern edge of the Guthrie quadrangle, for example, the top of the conglomerate of Bonita Creek is marked by a thin basalt flow that is correlated with a thick sequence of flows farther south that have been dated at 16.6 and 16.2 Ma (Richter et al., 1981). To the north and east of lower Eagle Creek, tuffs are not present within the upper part of this unit, and its upper contact is defined by the initial appearance of rhyolitic clasts in the conglomerate. Sequence 5 also includes thin basaltic andesite lava that overlies the 22.25 Ma Ttt unit of Richter et al. (1983) in the Guthrie Peak area.

Sequence 6 (19 to 17 Ma) Younger rhyolites of the northern Peloncillo Mountains: A series of rhyolite lava domes are present in the northern Peloncillo Mountains, but they are not separated from the older rhyolitic lavas by any significant thickness of sedimentary rock. Richter et al. (1983) dated one lava dome at 17.3 Ma, and a distal tuff interbedded
with the unit of Bonita Creek (map unit Ttt) along lower Gila River at 19.1 Ma. Sanidine phenocrysts from one of these lava domes were dated for this study and gave a 17.9 Ma age. Map units of Richter et al. (1983) that correlate with this sequence are Ttd, Ttv, Ttb, Trp, Trb, and Trd.

**Sequence 7 (18 to 12? Ma) Conglomerate of Midnight Canyon:** A succession of heterolithic conglomerates that contain sub-equal amounts of basalt and rhyolite lava and tuff clasts occur in the San Francisco, Eagle Creek, and Duncan basin areas around the Clifton-Morenci area, and in Pigeon Creek to the north of the map area. Rocks of this sequence, also mapped as unit Tgmc, occur southwest of the map area in the Bonita Creek area (Richter et al., 1983), and on the west side of the Turtle Mountains in the northeast corner of the Safford quadrangle (Houser et al., 1985). This unit was mapped as rhyolite by Lindgren (1905a,b), as rhyolite conglomerate by Heindl (1960), and as QTg by Richter and Lawrence (1981). The basal contact is marked by thin tuff lenses (Ttt) dated at 18.2 Ma in this study in the southwestern portion of the map area where present, or by indistinct gradation into the basaltic conglomerate and andesite of the conglomerate of Bonita Creek (Tbck) below. The upper contact is conformable with the overlying unit of Buzzard Roost Canyon (Tgbr). Richter et al. (1983) assign a Miocene age for the Conglomerate of Bonita Creek in Sequence 5 and indicate that the Conglomerate of Midnight Canyon in the overlying Sequence 7 is late Miocene to Pliocene in age. Using the rhyolite tuff (Ttt) of Sequence 6 as a marker, deposition of Sequence 7 rocks began around 18 Ma and extended to an unknown time in the mid-Miocene (~12 Ma?), rather than to the Pliocene. $^{40}$Ar/$^{39}$Ar age dates (this study) from alunite in the Morenci deposit of 13.4 and 11.0 Ma suggest that
the volcanic rocks and some of the underlying Cretaceous, Paleozoic, and Proterozoic rocks had been stripped from the top of portions of the Morenci block by the end of the mid-Miocene. This detritus was deposited in the unit of Buzzard Roost Canyon of Sequence 8, described below.

**Sequence 8 (12? to 5? Ma) Unit of Buzzard Roost Canyon:** A succession of heterolithic conglomerates that contain clasts of basalt, rhyolite lava and tuff, Laramide-age porphyry, Paleozoic sedimentary rocks, and Proterozoic granite occur in the San Francisco, Eagle Creek, and Duncan basin areas around the Clifton-Morenci area. The units of Sequence 8 are correlated with the Tgre and Tgor units of Richter et al. (1983) and Houser et al. (1985) in the Guthrie and Safford quadrangles to the south and southeast of the study area. This unit was mapped as Quaternary gravels by Lindgren (1905a,b), as Qgcc and Qgsf by Pawlowski (1980), and included with unit QTg of Richter and Lawrence (1981). The Tgbr unit has a gradational lower contact that is marked by the first appearance of Paleozoic limestone or quartzite and typically 1-5% red granite clasts, and the abundance of non-volcanic clasts increases upwards to 15-30% at the top of the unit. In places the unit contains rare clasts of skarn and oxidized copper-sulfides in veined and altered porphyry and Proterozoic granite. Richter et al. (1983) and Houser et al. (1985) assign a Pliocene age to this sequence. However, the alunite age dates from this study, described above, suggest that rocks of Sequence 8 were probably deposited beginning at the end of the mid-Miocene (~12 Ma) and continuing into the early Pliocene.

**Sequence 9 (5? to 2 Ma) Unit of Smugglers Canyon:** A succession of heterolithic conglomerates that contain clasts of local provenance occur as an apron around the
Morenci block and as upper basin fill in the Duncan basin. They also occur in the Guthrie quadrangle (Richter, et al., 1983) along the northwest side of Guthrie Peak in the Duncan basin. This unit was included with the Quaternary gravels of Lindgren (1905a,b), as Qgsb by Pawlowski (1980), and with unit QTg of Richter and Lawrence (1981). The conglomerates of Sequence 9 contain highly variable amounts of locally derived red Proterozoic granite, volcanic rocks, Laramide porphyritic plutonic rocks, and Paleozoic sedimentary rocks. Clasts are weakly to strongly imbricated in places and may be rounded to sub-angular in shape, depending on proximity to source area. The unit contains <1 to 15% black polished hematite and magnetite clasts, and copper-oxide mineralized, veined, altered and leached clasts of skarn, porphyry, quartzite, and granite. This detritus continued to be eroded from the adjacent Morenci deposit, as were the rocks of unit Tgbr in Sequence 8. The formation of significant copper enrichment was completed by about 7 Ma and thick leached capping was exposed around 5 Ma, based on $^{40}$Ar/$^{39}$Ar age dates from alunite and jarosite in the Morenci deposit from this study. Base level drop and incision of the Gila River and its tributaries began cutting rocks of Sequence 9 in the early Pleistocene.

**Stratigraphy and Structure of the Duncan Basin**

The evolution of the Duncan basin is inextricably linked to evolution of the surrounding landscapes and ultimately to the evolution of supergene enrichment in the Morenci porphyry copper deposit. The history of erosion and unroofing of the adjacent bedrock blocks is recorded in the sediments and by the structure of the basin. Bedrock and
Stratigraphy

The stratigraphy of the Duncan basin generally conforms to the five categories of Anderson and his co-workers (1992, 1995) for the southeast basins (Figure 19). The stratigraphy of the Clifton-Morenci area below follows this convention.

**Bedrock of the mountains:** The Peloncillo, Big Lue, Summit, and Steeple Rock Mountains that surround the basin are composed chiefly of mid-Tertiary volcanic rocks. They range in age from about 34 Ma to around 18 Ma (Drewes et al., 1985; Morrison, 1965; Ratte and Brooks, 1995; Richter et al., 1983; Richter and Lawrence, 1981; Wahl, 1980) and include units of Sequences 1, 2, 3, 4, and 6. Limited exposures of Proterozoic granite, Paleozoic and Mesozoic sedimentary rocks, and Laramide-age felsic intrusive rocks occur north of the basin in the Morenci block of the Clifton-Morenci area as described in the Geologic Setting section above. The volcanic rocks described in the Unit Description and Volcanic Geochronology sections above surround the basin, are chiefly andesite to basaltic-andesite in composition, and comprise 80-90% of the volcanic sequences (Witcher, 1981). The remaining 10-20% of the rocks are rhyolitic to dacitic flows, tuffs, and breccias. Subordinate amounts of volcaniclastic rocks are interbedded with the volcanic sequences. The volcanic sequence is almost 4 km thick on the east (Wahl, 1980) and over 1 km (3,280 ft) thick on the west (Richter and Lawrence, 1981;
Richter et al., 1983), and represent overlapping assemblages from the Mogollon-Datil and Peloncillo volcanic fields in the Clifton-Morenci area.

**Pre-Basin and Range sediments:** Pre-Basin and Range sediments of probable lower Miocene age (Drewes et al., 1985) are poorly exposed along the margins of the basin. They crop out in the upper Apache and Bitter Creek areas along the northwest range-front of the Summit and Steeple Rock Mountains (Figure 11), near Ash Peak and Black Mountain in the Peloncillo Range, and along a segment of the Gila River, Eagle Creek, and the San Francisco River near their confluence at the western edge of the basin (Drewes et al., 1985). These rocks include the volcanic conglomerate and “tilted tuffaceous beds” of Heindl (1962) and the Miocene conglomerate of Bonita Creek of Richter et al. (1983) of Sequence 5.

**Lower basin fill:** Weakly to strongly consolidated gravel, sand, silt, and clay of Miocene to Pliocene age compose the lower basin fill in the Duncan valley. Lower basin fill is in fault contact with Precambrian, Paleozoic, and Mesozoic rocks at the northern margin of the Duncan basin in the lower San Francisco and Eagle Creek areas. Elsewhere, the lower basin fill is generally in depositional contact with the pre-Basin and Range sedimentary and volcanic rocks. The sediments of the lower basin fill are characteristic of the adjoining bedrock sources (Heindl, 1962) and are predominantly conglomerate with lesser amounts of sandstone and mudstone near the range-fronts. The conglomerate facies occur dominantly in the Eagle Creek and San Francisco sub-basins and in a one to three km wide zone along the northeast margin of the basin (Halpenney, et al, 1946; Morrison, 1965). Along the Peloncillo Mountains the conglomerate zone is narrow, and the coarse
conglomerate lenses of the rocks typical of the Peloncillo Mountains inter-finger with small-pebble conglomerate, sandstone, and mudstone derived from rocks similar in composition to those of the Big Lue Mountains (Heindl, 1962). Towards the center of the basin the lower basin fill grades into finer grained beds that further grade into lacustrine and playa deposits in the vicinity of Duncan. The thickness of the lower basin fill ranges up to 625 m (>2,000 ft) thick in the Clifton-Morenci area (this study) to almost 2 km (>6,000 ft) thick in the center of the basin (West, 1996). The lower basin fill is generally flat-lying with dips between 1-2° towards the axis of the basin and average dips of 9° to 11° in the San Francisco River and Eagle Creek sub-basins. The lower basin fill is correlative to the alluvial sedimentary beds of the “Gila Conglomerate” described by Gilbert (1875), Lindgren (1905a,b), Heindl (1958, 1962), and the “Gila Group” described by Crews (1994) and Richter et al. (1983). Lower basin fill includes the conglomerate of Midnight Canyon (Tgmc) of Sequence 7, the unit of Buzzard Roost Canyon (Tgbr) of sequence 8, and the unit of Smuggler Canyon (QTgs) of Sequence 9.

**Upper basin fill:** The upper basin fill is poorly represented in the Duncan basin. Tuffaceous sediments probably deposited in a lacustrine environment rest disconformably upon coarse-grained red beds near the center of the basin, in the vicinity of Duncan (Harbour, 1966). These deposits are likely of early Pleistocene age and may represent what exists of the upper basin fill in the Duncan valley. The thick deposits of upper basin fill in the Safford basin probably represent erosion in the Duncan basin (Harbour, 1966). The upper basin fill consists dominantly of poorly consolidated orange silt and contains interbeds of diatomaceous material and marly horizons in places (Heindl, 1962). Halite
and gypsum occur widely throughout the lacustrine facies of the upper basin fill (Halpenny, et al, 1946). The thickness of tuffaceous sediments of the upper basin fill is not well known, but may be on the order of 100 m (330 ft), based on descriptions of “clay” from drillers’ logs (Feth, 1952). The Older Alluvial Deposits (QTao) in the surrounding Eagle Creek and San Francisco sub-basins may represent the remnants of upper basin fill the Clifton-Morenci area.

**Stream alluvium:** A series of seven graded Pleistocene and younger surfaces that slope toward the interior of the valley have cut into the upper and lower basin fill (Morrison, 1965). Distinct scarps usually border the floodplains of the present streams and rise 15 m (50 ft) to 30 m (100 ft) to one or more of the higher erosional surfaces that form the inner valley. These are fairly wide in to the south in the Duncan and Virden areas, but give way to spectacular inner gorges in the lower reaches of the Gila River, Eagle Creek, and the San Francisco River canyons. Stream alluvium (Qa, Qao) consisting of unconsolidated gravel, sand, and silt of channel, point bar and floodplain deposits fills the inner valleys to depths ranging from 1 to 50 m (3 to 164 ft).

**Clast counts and provenance:** The unroofing history of the adjacent bedrock is recorded in the clasts of the sediments in the basin fill. Relative clast count data collected during this mapping project are summarized in Table 8 and illustrated in a suite of ternary diagrams in Figure 20.

The lower conglomerate (Tcl) is the oldest mid-Tertiary sedimentary rock in the Clifton-Morenci area. Precambrian and Paleozoic clasts dominate and compose about 70% of the clasts. The remaining clasts are composed of 20% porphyritic intrusive rocks
and only 10% or less of volcanic lithologies including Clifton Tuff. Although there are some andesite clasts in the lower conglomerate, it is uncertain whether or not these are Paleocene-Cretaceous or mid-Tertiary in age (Wahl, 1980). The shale clasts probably represent both the Devonian Morenci shale and the younger Cretaceous Pinkard Formation. No mineralized or hydrothermally altered intrusive rocks were found in the lower conglomerate.

In general, clast compositions are dominated by volcanic lithologies in the late-Oligocene, Miocene and Pliocene units (Tbs, Tvs, Tbck, Tgmc, and Tgbr) and reflect the relative proportions of andesitic and rhyolitic rocks of their provenance areas. Andesite and basalt represent over 70-vol.% of the clasts. These rocks undoubtedly have a provenance in the surrounding basaltic andesites (Tb) in the Black Hills/Turtle Mountain areas of the northern Peloncillo range, but no attempt was undertaken to look at this in more detail. Rhyolite clasts peak in the conglomerate of Midnight Canyon (Tgmc) at 46% and indicate a provenance of Enebro Mountain Formation and similar age rocks in the Peloncillo and Black Lue Mountains during that period of time. Rhyolite clast abundance steadily drops to less than 10% by the Pleistocene (QTgs = 13%, QTao = 3%).

The contact between Midnight Canyon (Tgmc) and Buzzard Roost (Tgbr) is marked by the first appearance of Paleozoic limestone or quartzite and typically 1 to 5% red granite which grade upwards to 15-30% of the total volume of clasts. Diorite porphyry (Tpd) and monzonite porphyry (Tpm) compose about 23% of the total clasts in the Buzzard Roost. In places a few clasts to as much as 5% of the total clasts are mineralized and
altered. Some clasts contain malachite and chrysocolla. Others are skarn-altered and contain epidote replacing the original limestone. Some of the monzonite porphyry and Proterozoic granite clasts contain quartz-sericite alteration and stockwork veining. This clearly points to a Morenci block provenance for some of sediments that comprise the unit of Buzzard Roost Canyon.

Clast compositions in the unit of Smuggler Canyon (QTgs) and younger units reflect a very local provenance. In general, Precambrian and Paleozoic rocks increase in abundance at the expense of the intrusive porphyries. However, diorite porphyry comprises 100\% of unit QTgd in the Southwest Stockpile area at the southern end of the Morenci block adjacent to the diorite porphyry stock. In the upper San Francisco River canyon, typically unaltered and unmineralized, red Proterozoic granite composes 100\% of unit QTgg and forms the large alluvial fans along the hanging wall side of the San Francisco fault. In places the younger sediments contain variable amounts up to 15-20\% of black polished hematite and magnetite clasts, and copper-oxide mineralized, veined, altered and leached clasts of skarn, porphyry, quartzite, and granite.

Structure

The structure of the Duncan basin is complex but generally conforms to Anderson’s (1992) description of the southeastern Arizona basins as illustrated on the cross section in Figure 19. The Duncan basin is distinctly bounded on the west by a set of 040° striking, step-like normal faults (Figures 8 and 11). These basin-bounding structures dip steeply towards the basin at 75° to 85° and are exposed continuously for about 24 km along the
northeastern margin of the basin. The Ward Canyon fault southeast of Clifton bounds the northeastern margin of the basin for about 8 km (5 mi). These structures link up with the Eagle Creek fault system to the northwest and are cut by the northeast-striking faults of the San Francisco system to the northeast. From Guthrie to Duncan the Gila River hugs the western margin of the basin along the Peloncillo range-front. South of Apache Creek, the basin-forming structures are either poorly exposed or buried by basin fill, and their presence has been inferred from gravity and aeromagnetic data (Drewes et al., 1985; West, 1996) as shown in Figure 21.

Geophysical evidence: The Duncan basin is filled with low-density, generally non-magnetic sediments that provide a strong contrast to the high-density, magnetic mid-Tertiary volcanic rocks. This contrast provides insight into the internal structure of the basin. The simple Bouguer gravity anomalies show lateral density changes between basin fill and the mid-Tertiary volcanic rocks as short wavelength anomalies (Figure 21a). Aeromagnetic data over the Duncan basin show changes in the depth to the top of the volcanic rocks as short wavelength anomalies near the surface and by longer wavelength anomalies over successively down-faulted blocks (Figure 21b). Shadow maps of the aeromagnetic data are similar to horizontal directional derivative maps of the aeromagnetic data (West, 1996) and clearly show the location of the basin (Figure 21c). West’s (1996) structural interpretation of the gravity and aeromagnetic data for the Duncan basin resulted in a significantly different interpretation of the thickness of basin fill than the previously published estimates of 300 m (Halpenny, et al., 1946; Heindl, 1962; Remick, 1989) and 900 m (2,950 ft) (Feth, 1952), as discussed below.
Geophysical and drill hole data show the basin to be separated into segments with very different depths. West’s interpretation of the gravity data (Figure 21d) indicates that basin depth decreases from 1,800 m (>6,000 ft) at its northwest end near Clifton to 760 m (2,500 ft) near Duncan. This is corroborated by drill holes in the Tailings Dam area south of the Morenci block. In this area, an isopach map of basin fill thickness (Figure 22) shows steep gradients to the northeast along the hanging wall of the Ward Canyon fault. No evidence exists for a fault of the magnitude of the Ward Canyon fault in the Morenci block. The Ward Canyon fault is buried by the upper sediments of the unit of Buzzard Roost Canyon and is presumed to continue on a more westerly strike south of the Morenci block. The map also reveals that the basin margin has steep gradients adjacent to the San Francisco fault that continue west towards the Eagle Creek fault. Basin depths exceed 900 m beneath the Tailings Dam area. In the vicinity of Franklin, Arizona, an inferred, north-south-striking, normal fault coupled with northeast and northwest-striking segments are coincident with a change in the alignment of the Gila River and increase the basin depth to 1,800 m (>6,000 ft). Further to the south, another normal fault, striking east-northeast, causes the basin depth to decrease to 600 m (2,000 ft). Magnetic lineaments suggest that several step faults and cross faults also occur in addition to the major normal faults (West, 1996).

**Eagle Creek sub-basin:** The major structural features of the Eagle Creek area are northwest-striking normal faults that define a relatively shallow graben. The Eagle Creek fault dips 65° to the southwest and strikes approximately 305°. It bounds the graben on the east side from the intersection with the Coronado fault to the northwest, a distance of 9 km
(5.5 mi) to the southeast, before being lost under the Southwest stockpiles and sediments of unit Qtgd. Further to the north, the Eagle Creek fault changes strike to 330° and exits the map area. A series of sub-parallel, anastomosing northwest-striking normal faults define the western half of the graben. A master fault separates a thick succession of andesite flows (Tb) from conglomerates of Bonita Creek (Tbck) and Midnight Canyon (Tgmc) (Figure 22, Plate 1). These structures extend to the southeast and pass through the confluence of the Gila and San Francisco Rivers and define the northwest margin of the Duncan basin. Many of the faults are not traceable into the conglomerates and sandstones of units Tgbr. This relationship provides a relative indication of the timing of the structural development of the Eagle Creek sub-basin. Dip directions of the basin fill define a broad south-plunging syncline along the upper reaches of the Eagle Creek valley adjacent to the Morenci block that may have been formed as drag folding on the Eagle Creek fault or as a result of growth faults during sedimentation. The Eagle Creek fault appears to cut all units older than QTgd but is overlapped in places by sediments of QTgd. Drill holes (Appendix C) in the hanging wall indicate at least 1,160 m (3,800 ft) of vertical separation along the Eagle Creek fault (Phelps Dodge, 1969; Walker, 1995) as shown in cross section A-A’ (Figure 23) and on Plate 2. Stratigraphic thickness from drill holes (Figure 22) and outcrops (Appendix C) show maximum thicknesses of the basin fill between 500 m (1,640 ft) and 600 m (1,970 ft).

**San Francisco sub-basin:** The major structural features of the upper San Francisco River area are the northeast-striking normal faults that define the western margin of a westward-dipping half-graben. The San Francisco fault has an average strike of 030-040°
and an average dip of 70° to the southeast. It extends for over 21 km (12.8 mi) from the south, where it is covered by mine tailings, to where it exits the map area and continues on to the northeast. The fault is defined by a master fault and at least three subsidiary faults at the range front that offset basin fill and older units in the hanging wall against Proterozoic granite and granodiorite of the Malpais-San Francisco horst. Just northwest of Clifton, drill hole data (Figure 24, and cross-section D'-D", Plate 2) show that the San Francisco fault must have a steep (greater than 75°) easterly dip. However, at several localities along the surface trace of the fault farther north, major strands of the fault are exposed that have moderate (less than 60°) easterly dips. Relationships preserved where the San Francisco fault crosses Sardine Creek in the northeast part of the map suggest that a younger, steeply dipping strand cuts an older, moderately east-dipping strand. This relationship is depicted somewhat hypothetically on all of the east-west structural cross-sections on Plate 2. The San Francisco fault appears to cut all of the older northwest-striking faults. Dip directions of the basin fill and older volcanic rocks define a series of broad, northwest-striking synclines in the upper reaches of the valley. These may have been formed as drag folding along the San Francisco fault, or as a result of some right-lateral movement along the fault as postulated by Walker (1995); however, no strike-slip indicators are evident along the exposed fault surfaces. Drill holes (Appendix C) in the hanging wall indicate at least 915 m (3,000 ft) of dip-slip separation along the San Francisco fault (Phelps Dodge, 1982; Walker, 1995) as shown in cross section B-B''' (Figure 24). Stratigraphic thickness from drill holes (Figure 22) and outcrops (Appendix
C) show maximum thicknesses of the basin fill between 500m (160 ft) and 625 m (2,050 ft).

A prolonged history of normal faulting is evident east of San Francisco fault north and east of Clifton. Directly east of Clifton, Cunningham (1981) shows numerous east-side-down normal faults cutting Paleozoic units that apparently do not cut the overlying basal Tertiary succession of Clifton Tuff and basaltic andesite lava. To the north of Clifton, there is evidence of faulting during the Oligocene in at least two areas. Near its southern termination in lower Limestone Gulch, a splay of the major northeast-striking fault in Limestone Gulch offsets 34 Ma Clifton Tuff, but is apparently overlapped by the 29 Ma Bloodgood Canyon Tuff. Farther northeast, the main strand of this fault zone cuts the lower part of the basaltic andesite map unit (Tb), but is clearly buried by the upper part of the same sequence. Both parts of the basaltic andesite sequence have been dated at approximately 27 Ma. Fault intersections are complex near the mouth of Limestone Gulch, but it appears that the basal sedimentary rocks of the Gila Group overlap a main, southeast-side-down strand of the fault system in Limestone Gulch just to the west of San Francisco River.

Related faults of the Morenci block: The Morenci block includes a number of major, mostly east-side-down and south-side-down normal faults that mimic the orientations and kinematics of the major faults that bound the block to the southwest and southeast (Plates 1, 2, and 3). Detailed studies of some of the fault zones indicate a prolonged Tertiary history of motion (Walker, 1995). The faults are well exposed around the periphery of the main mineralized district, and stratigraphic offsets are well
documented in the Phanerozoic supracrustal sequence that occurs in the area. However, these faults either lose displacement or are lost in the intrusive complex in the center of the district. The Quartzite, Coronado, and Producer faults are major south- or southeast-side-down structures that die out or transfer displacement towards the center of the district. A more detailed map of the faults in the central portion of the Morenci district is shown in Figure 10.

The major, east-side-down Chase Creek fault in the north-central part of the district mimics the San Francisco fault in orientation and displacement. Maximum stratigraphic offset across Chase Creek fault is about 310 m (1,017 ft) (Walker, 1995). The Chase Creek fault strikes due north, makes a dogleg jog to the north-northeast where it leaves Chase Creek, and splays into a southwest-side-down fault that dies out to the northwest near the head of Chase Creek (Plate 1). The main strand continues north-northeast to a major northeasterly dogleg turn at Pigeon Creek just to the north of the study area. This is at the same latitude as a similar northeast turn in the San Francisco fault. The Chase Creek fault cuts units as young as the Gila Group where it leaves the study area to the north. At its southern end, it appears to have acted as a transfer zone for displacement along the south-side-down, Coronado, Producer, and Quartzite faults (Figure 10). The southern end of the Chase Creek fault is poorly understood, but it may die out within the intrusive complex in the central part of the district or transfer displacement to the east-side-down Las Terrazas, Apache, or Copper Mountain faults (Figure 10).

The Garfield fault is the northernmost east-west striking fault in the Morenci block, and the only major north-side-down fault in the district. Its greatest displacement is in the
immediate hanging wall of the Chase Creek fault. The Garfield fault dies out to the east near Copper King Mountain, but continues west of the Chase Creek fault into a poorly understood termination in the upper Eagle Creek drainage basin (Plate 1). Although it is clear that the Garfield fault does not offset the Chase Creek fault, the exact location of the eastern end of Garfield fault in the footwall of the Chase Creek fault is not known, because the footwall is composed of homogeneous Proterozoic granite. The Garfield fault is shown on Plate 1 offset slightly in an apparent dextral sense, a pattern which is consistent with purely dip-slip, east-side-down offset across the Chase Creek fault. Although strike-slip indicators have been documented along some of the faults in the Morenci block (Walker, 1995, Parker, pers. commun.), there is little evidence of major strike-slip offsets along any of the faults, and the apparent strike-slip offsets can be accounted for by normal dip-slip motions.

**Dip data:** Measured dip angles for the strata in the Clifton-Morenci record the structural evolution of the area (Table 9). In general, the Paleozoic sedimentary and mid-Tertiary volcanic rocks tilt gently westward between 5° and 40° and average about 20° in several tilt blocks. The sedimentary rocks of the basin fill displays fanning dip sequences that progressively flatten from an average of about 21° in the early-Miocene Enebro Mountain Formation (Te) and conglomerate of Bonita Creek (Tbck) to essentially flat-lying in the Pleistocene and younger sediments. Overall, the change in dip angles from about 21° to 11° marks the unconformity and break between early-Miocene volcanism and the basin sedimentation; however, the units appear to be locally conformable. Dips gradually flatten through Miocene and Pliocene time to an average of only 4° in the unit of Smuggler Canyon
In general, dips are steeper in the Eagle Creek area and become shallower south towards the center of the Duncan basin.

Discussion

Mid- to late-Tertiary erosion, tectonism, and associated volcanism and sedimentation played a profound role in the formation and preservation of supergene enrichment in the Morenci porphyry copper deposit. The evolution of the Cenozoic landscape and associated supergene enrichment in the Morenci district can be divided into five stages: 1) formation of the porphyry copper deposit at about 55 Ma, 2) initial unroofing and mechanical weathering during the first erosional period between ~53 and ~29 Ma, 3) subsequent preservation under volcanic cover between ~29 and 18 Ma, 4) re-exposure and chemical weathering during the second erosional period between ~13 and ~4 Ma, and 5) further base-level drop and stream incision during the third erosional period. Most of the supergene enrichment at Morenci appears to have been formed in the fourth stage during episodic uplift and basin subsidence as a result of Basin and Range deformation between ~13 and ~4 Ma. The results of this study are illustrated on the time-space diagram in Figure 25, and the stages are described below.

Stage 1 - Initial Depth of Burial (64 to 53 Ma)

Estimates of depths of hydrothermal processes, under hydrostatic conditions, from fluid inclusion studies (Preece, 1986; Holick, 1998) indicate that a minimum thickness of 1.7-1.9 km (5,600-6,200 ft) of cover must have buried the deposit during its hydrothermal
evolution. The total thickness for the Paleozoic section is 324 m (1,063 ft) and the minimum thickness for the Mesozoic Pinkard Formation and Ft. Crittenden-equivalent section is 238 to 430 m (780 to 1,410 ft). This accounts for only 562 to 754 m (1,843 to 2,473 ft) of cover. However, there is evidence from nearby areas that indicates that a greater thickness of Cretaceous rocks could have been present in the Clifton-Morenci area prior to Laramide intrusive activity. Approximately 53 km (32 mi) to the southeast near Virden, New Mexico, Kottlowski (1963) reported a thickness of 244 m (800 ft) for the Colorado Formation that is correlative with the Pinkard Formation. In addition, he described 1,220 m (4,000 ft) of Cretaceous sedimentary and volcanic rocks of the Virden Formation that unconformably overlie the Colorado Formation in that area. He further showed that the Upper Cretaceous rocks of Arizona and New Mexico have been removed by erosion along a margin trending roughly east–west and passing 22 km (13.4 mi) north of Morenci. If the full section of Cretaceous rocks from Virden were present prior to erosion at Morenci, then the total Paleozoic and Mesozoic cover would have been 1,782 to 1,974 m (5,845 to 6,475 ft). The pre-mineral volcanic sequence in the Safford area is about 823 m (2,700 ft) thick near the Lonestar and Dos Pobres deposits (Robinson and Cook, 1966) and ranges up to 1,700 m (5,576 ft) in the Safford quadrangle (Houser et al., 1985). If a similar section of Cretaceous volcanic rocks were present above the Morenci intrusive center, then the total Paleozoic and Mesozoic cover could have been from 2,262 to 2,454 m thick (7,419 to 8,050 ft). Preece, Stegen, and Weiskopf (1993) concluded that a coeval andesitic volcanic pile must have attended Laramide intrusive activity to account for their
estimates of depths of burial. How much of this cover was mineralized remains open to conjecture.

Stage 2 - First Erosional Period (53 to 30 Ma)

The Morenci block and copper deposit were exposed and subject to erosion from their formation between ~57 to ~53 Ma and the onset of mid-Tertiary volcanism between ~34 to ~30 Ma. With the exception of the lower conglomerate, recent mapping during this study failed to find any evidence for Eocene or Oligocene sedimentary rocks from the first mid-Tertiary erosional period in the Clifton-Morenci area. Presumably, the Laramide volcanic rocks and portions of the underlying formations that were eroded from the deposit, were transported and deposited to the north in the Eocene Baca basin of west-central New Mexico and east-central Arizona (Walker, 1995). During this period, the Morenci uplift was part of the broader Mogollon Highlands that shed detritus including abundant volcanic clasts to the northeast (Cather and Johnson, 1984; Pierce et al., 1979).

Dissection of this terrain began in early-Oligocene time when new drainages were created south of the Mogollon Rim in response to uplift that brought the Colorado Plateau edge from sea level to its present elevation (Scarborough, 1989). This was accompanied by widespread extensional deformation and initiation of arc magmatism (Dickinson, 1989). In the Clifton-Morenci area, the Clifton Tuff (~34 Ma) of Sequence 1 is the oldest known mid-Tertiary volcanic rock. The Clifton Tuff was deposited on the western edge of the Mogollon-Datil volcanic field during the first pulse of ignimbrite volcanism (McIntosh et al., 1992). This unit is exposed in Clifton and other locations in the upper San Francisco
River valley, and it has been encountered in drill holes in the hanging wall of the San Francisco fault (Figure 24) adjacent to the Morenci block, but not further to the west. Presumably, Clifton Tuff was deposited on partially eroded Paleozoic rocks in portions of the southeastern side of the Morenci block, and arrested supergene processes in those areas.

The lower conglomerate (Tcl) of Sequence 1 represents the last significant period of erosion and sedimentation prior to the main pulse of late-Oligocene and early-Miocene volcanism. These rocks are correlative with the Whitetail Assemblage of Scarborough (1989). Clast compositions indicate that the Morenci block was shedding detritus on to the surface of the Clifton Tuff in adjacent local basins. The detritus included some of the Clifton Tuff as well as the sedimentary and plutonic rocks of the adjacent bedrock blocks.

Although erosion had exposed the Laramide-age porphyries, there is no evidence to substantiate whether or not these rocks contained any hydrothermal alteration or hypogene copper mineralization. The basaltic andesite (28.82 Ma) at “Tv Hill”, south of the Coronado fault on the western edge of the deposit, intrudes and rests unconformably on skarn altered rocks of the Ordovician Longfellow Formation and Cambrian Coronado Quartzite at an elevation of 1,850 m (6,070 ft). Some of the copper deposit thus had an opportunity to be leached and enriched by this point in time. However, there is no hard evidence of a pre-Miocene enrichment period in the deposit (Cook, 1994), and there are no copper-bearing or hydrothermally altered clasts in the lower conglomerate. Assuming an initial thickness of 1.8 km (5,900 ft) above the pre-volcanic erosional surface and a 24
milllion-year period (~53 to ~29 Ma), the erosion rate during this period averaged 0.08
mm/yr. (0.0031 ft/yr.).

Stage 3 - Mid-Tertiary Volcanic Cover (30 to 18 Ma)

The Clifton-Morenci area was covered by a succession of volcanic rocks of
Sequences 2 through 6 beginning at about 29 to 30 Ma or even as late as 27 to 28 Ma.
Evidence for this includes the andesite dike at Metcalf dated at 30 Ma (Cook, 1994) and
from the andesite at “Tv Hill” at Coronado dated at 28.52 Ma (this study), as well as the
voluminous andesitic lavas in the adjacent blocks. The western pinch-out of the
Bloodgood Canyon Tuff (28 Ma) appears to be along the eastern side of the Morenci block
suggesting that this area was still a highland up until ~28 Ma. Andesitic volcanism
occurred dominantly from 30 Ma to about 23 Ma with peaks around 24-25 Ma and 27-28
Ma. Rhyolitic volcanism periodically punctuated this regime with eruption of the Clifton
Tuff (~34 Ma), Davis Canyon Tuff (~29 Ma), Bloodgood Canyon Tuff (~28 Ma), and a
succession of younger tuffs from 24.5 Ma to 18.2 Ma. Volcanic assemblage sediments of
Scarborough (1989) include thin volcaniclastic and tuff layers of unit Tbs which represent
short erosional and depositional breaks during this time. Mid-Tertiary volcanic cover
over the Clifton-Morenci area ranged from about 640 m (2,100 ft) in the northern areas to
over 950 m (3,120 ft) in the southern areas of the Morenci block. This volcanic cover
preserved the Morenci porphyry copper deposit from further erosion until the early
Miocene and protected the deposit from continuing supergene processes.
Stage 4 - Second Erosional Period (18 to 2 Ma)

Basin subsidence began in the Clifton-Morenci area during the waning stage of volcanism sometime between ~24 and ~22 Ma and marks the initiation of erosion of the surrounding bedrock blocks. Basin subsidence appears to have started slightly earlier in the east. In the San Francisco River area, tuffs associated with the Enebro Mountain Formation (22.25 to 20.6 Ma) of Sequence 4 are interlayered with basaltic conglomerate (Tcb) and with the conglomerate of Midnight Canyon (Tgmc) of Sequence 7. In the Eagle Creek area, tuff beds (Ttt) ranging in age from 19.1 and 18.2 Ma of Sequence 6 at the top of the conglomerate of Bonita Creek mark the base of the conglomerate of Midnight Canyon (Tgmc). Further to the east in the Big Lue quadrangle, basalt flows ranging in age from 19.1 to 17.7 Ma. are also interlayered with sedimentary rocks of the Gila Group (Ratte and Brooks, 1995). The relative timing of Mid-Tertiary extension is also reflected in the thickness of volcanic rocks encountered at depth in drill holes in the hanging walls of the basin-bounding faults. In the hanging wall of the Eagle Creek fault, 600 m of basaltic andesite (Tb) flows are sandwiched between lower basin fill and Pinkard Formation (Figure 23). This indicates approximately 350 m (1,150 ft) of overlying volcanic rocks had been eroded prior to faulting. In the hanging wall of the San Francisco fault, 325 m (1,066 ft) of basaltic andesite and Clifton Tuff are sandwiched between lower basin fill and Modoc Formation. Midnight Canyon conglomerates contain only volcanic clasts. This unit is very widespread and occurs extensively to the southwest in the Safford basin (Kruger et al., 1995), and to the north of the Morenci block in the Pigeon Creek and HL
Canyon areas. Sedimentary rocks of Midnight Canyon represent fluvial conglomerates of proximal alluvial fans adjacent to the bedrock blocks (Kruger et al., 1995).

Erosion of the bedrock blocks and episodic basin subsidence continued through Miocene and Pliocene time. Major faulting associated with Basin and Range deformation began in the region between 13 and 10 Ma and probably continued up to about 6 Ma (Menges and Peartree, 1989). At this point, the modern regional drainage patterns were established (Scarborough, 1989). The second erosional period appears to have been the most significant period for supergene enrichment at Morenci, based on \(^{40}\)Ar/\(^{39}\)Ar age dates from alunite dated between 13.4 and 4.3 Ma (this study) and the sedimentary record in the rocks of the Duncan basin. During this period, the remaining volcanic rocks were eroded from the Morenci district and the mineralization was exposed to supergene processes.

Sedimentary rocks of the unit of Buzzard Roost Canyon (Tgbr) of Sequence 8 appear to be conformable with the underlying Midnight Canyon conglomerates and contain dominantly volcanic clasts at the base. Higher in the section the sedimentary rocks progressively record the unroofing of the Morenci block. At the top, the unit of Buzzard Roost Canyon contains 15-30% non-volcanic clasts and up to 5% altered and mineralized clasts in some locations. The unit is restricted to the Duncan basin. The less indurated, finer grained character and greater degree of sorting and bedding in the Buzzard Roost sediments indicate fluvial conditions with longer periods of sustained flow. Assuming an initial thickness of 950 meters (3,120 ft) of cover over the Morenci district and an 8 million-year period (~18 to ~10 Ma), the erosion rate during this period averaged 0.12 mm/yr. (0.0047 ft/yr.), or about 1-1/2 times the rate during the first erosional period.
Stage 5 - Third Erosional Period (2 Ma to present)

Renewed erosion and base level drop accompanied down cutting of the Gila River during Pleistocene time. This was a result of progressive drainage integration in southern Arizona that began during Pliocene and Pleistocene time as a result of migrating drainage divides, diversion by stream piracy, and basin in-filling overtopping divides (Menges and Pearthree, 1989). Drainage in the Duncan basin was captured and integrated with the Safford basin during the early or middle Pleistocene (Harbour, 1966). Progressively greater amounts of mineralized and altered rocks including leached capping from the Morenci deposit occur in the overlying sediments of the unit of Smuggler Canyon (QTgs) of Sequence 9 and Older Alluvium (QTao). These units occur predominantly to the south and east of the Morenci block and record the most recent erosion from adjacent rocks. Sediments of the unit of Smuggler Canyon contain interbedded silt, sand, and conglomerate lenses that indicate fluvial conditions in a lower energy environment and lower stream gradients associated with nearly full conditions in the Duncan basin. Based on the distribution and sedimentary facies in this unit, it is likely that integration was the result of basin filling and overtopping. The Gila River, Bonita Creek, Eagle Creek, and the San Francisco River deeply incised their drainages during this time. The inner gorge of these canyons ranges from 200 m (650 ft) to over 315 m (1,030 ft) deep which is consistent with the extent of drainage dissection elsewhere in the region. The Chase Creek drainage was probably integrated into the San Francisco River at this time. Assuming down cutting
began around 1 Ma, the erosion rate during this period averaged 0.25 mm/yr. (0.010 ft/yr.) or about double the rate during the second erosional period.

This sudden drop in base level stranded much of the enriched blanket at Morenci above the water table. This resulted in erosion of leached capping above the blanket in topographically low areas at Morenci, for example, and partial leaching of secondary sulfides along structures and at the top of the enriched blanket at Metcalf, for example. This process continues today. Leaching and exotic copper deposits as copper-manganese-iron–oxide-cemented gravel and bedrock are evident in the Chase Creek, Gold Gulch, Rocky Gulch, and Rockhouse Canyon drainages.
GEOLOGY, HYDROTHERMAL ALTERATION, AND MINERALIZATION OF THE MORENCI PORPHYRY COPPER DEPOSIT

Introduction

This chapter provides an update of the geology of the Morenci porphyry copper deposit with a focus on the formation of hypogene alteration and mineralization based on studies conducted over the last 25 years. The last widely published descriptions of the Morenci district are from Moolick and Durek (1966) and Langton (1973) when the district was focused only on the Morenci and Metcalf areas. To avoid repetition, this chapter begins with a description of the host rocks and structure of the Morenci porphyry copper deposit, followed by a description of the hydrothermal alteration and mineralization. The site conditions, previous work, and regional geology are presented in the previous chapters and not repeated here. Additional information about the distribution and characteristics of the hypogene zone, however, is included with appropriate sections of the next chapter, as a basis for an outcome of studies of the supergene zone.

The geology of the Morenci district is shown in a series of maps and cross sections. Figure 26 is a simplified geologic map of the district showing the Laramide intrusive complex and principal host rocks, and Figure 27 is a map showing the accompanying hydrothermal alteration. A suite of maps at a larger scale shows the geologic setting in the center of the district and are referenced throughout the rest of this dissertation. Figure 28 is a map of the host rocks in the pit area. Figure 10 shows the principal structures and Figure 29 shows the hydrothermal alteration of the same area. Figures 30, 31, and 32 are a set of cross-sections through the district that show the geology
and mineralization for the principal mineralized areas. The cross sections have been vertically exaggerated by a factor of 2.5 to 1 to emphasize the enrichment profiles. Figure 30 is a north-looking cross section along 12,000N through the American Mountain, Morenci, and Western Copper areas on the southern side of district. Figure 31 is a north-looking cross section along 16,000N through the Coronado, Northwest Extension, and Metcalf areas in the center of the district. Figure 32 is a west-looking cross section along 10,000W from Garfield through Shannon, Metcalf, Western Copper, and Morenci on the eastern side of the district.

**Host Rocks**

The host rocks for mineralization in the Morenci district are briefly described below (Figures 26 and 27). For detailed descriptions of the Precambrian, Paleozoic, and Mesozoic rocks, see Lindgren (1905a,b), which remains the best reference for these units. For detailed descriptions of the Laramide intrusive rocks see Bennett (1975), Menzer (1980), Preece and Menzer (1992), Griffin, Ring and Lowery (1993), Walker (1995), Phelps Dodge (1996b), and Wright (1997). Detailed descriptions including the mid-Tertiary through Quaternary volcanic and sedimentary rocks are also included in Ferguson and Enders (2000), and in Appendix A.

**Pre-Laramide Host Rocks**

Precambrian, Paleozoic, and Mesozoic plutonic and sedimentary rocks compose the country rock into which the Laramide porphyries were intruded. These rocks are
shown in the stratigraphic column in Figure 9, and are briefly described in the section on
the stratigraphy of the Morenci block in the previous chapter.

Laramide Intrusive Complex

A suite of calc-alkaline hypabyssal rocks intruded the Morenci block during the
Laramide orogeny (Figure 26). The stocks, laccoliths, and associated dikes and breccias
range from Paleocene to early Eocene in age (64.7 to 52.8 Ma) and in composition from
diabase to diorite, monzonite and granite (Moolick and Durek, 1966; Preece and Menzer,
1992; Griffin, Ring and Lowery, 1993, Walker, 1995). The central intrusive complex is
over 13 km (8 mi) long and 4 km (2.5 mi) wide and consists of a roughly north-south
alignment of elongate stocks and associated northeast-striking dike swarms. Hornblende-
bearing diorite porphyry is the oldest Laramide intrusive rock in the district (~64 Ma);
except for minor skarn and hornfels alteration of the adjacent sedimentary rocks, it is
largely unaltered and unmineralized. The monzonite porphyry, older granite porphyry, and
younger granite porphyry intrusive complexes are the principal intrusive host rocks for
porphyry copper mineralization along with small bodies of Laramide-age diabase that
locally host copper mineralization.

The altered and mineralized porphyries are tonalite, granodiorite, and quartz
monzonite in composition, although normative compositions range from granodiorite
through quartz monzonite (Preece and Menzer, 1992). IUGS rock classifications (IUGS
sub-commission, 1973) used in this dissertation are based on normative and modal
interpretations reported in Preece and Menzer (1992), Griffin, Ring and Lowery (1993),
and Walker (1995), but without supporting data. Plagioclase typically occurs in the groundmass and as phenocrysts of oligoclase to andesine, but orthoclase is generally restricted to the groundmass. Traditionally, these host rocks have been mapped on the basis of the abundance and size of quartz phenocrysts. This ranges from rare quartz phenocrysts in monzonite porphyry and to 3-10% in the older and younger granite porphyries. Extensive mineralization, and hydrothermal and supergene alteration, most commonly as abundant quartz-sericite-pyrite stockwork veining and pervasive alteration, obscure the original texture and chemistry of these rocks.

Several breccia bodies are part of the intrusive system in the district. The breccias are variably altered and mineralized and were developed during two periods of brecciation (Bennett, 1975). These include the Morenci and Candelaria breccias that cut the older granite porphyry complex, and the Metcalf and King breccias that appear to be related to the younger granite intrusive complex.

Laramide intrusive activity may have been associated with a coeval, overlying andesitic stratovolcano (North and Preece, 1993; Preece, Stegen and Weiskopf, 1993). However, no physical evidence of such volcanic rocks has yet been discovered.

**Structure**

Several deformational periods controlled the intrusions, mineralization, and structures in the complex terrain of the Morenci district. Overall, the district displays a series of east-west-striking, northwest-striking, northeast-striking, and north-south striking normal faults some of which were Laramide-age or older structures that were re-activated
during mid-Tertiary, and Basin and Range deformation (Walker, 1995). Although many of these faults are not easily traceable through the intrusive complex, they have dislocated the district into several discrete domains.

**Laramide-age Structures**

Regional tectonism during the Laramide orogeny exerted a strong control on the distribution of the intrusions, faults and veins in the Morenci district. Structural orientations of individual vein sets and dikes record a systematic change in the stress fields during the Laramide orogeny (Preece, Stegen and Weiskopf, 1993). The radial orientation of dikes, and the sills and laccoliths in the diorite porphyry and the variable orientation of the early stockwork veinlets suggest that a local stress field dominated the Morenci area early in the Laramide orogeny. The orientation of the monzonite porphyry dikes range from $050^\circ$ to $070^\circ$, and are conformable with the most common regional Laramide orientation in the porphyry copper deposits of the southwestern U.S. (Heidrick and Titley, 1982). The orientation of the older granite porphyry dikes, late-stage fissure veins, and many of the Laramide-age normal faults in the district range from $020^\circ$ to $040^\circ$ and record a shift in the northwest to north-northwest extension direction late in the Laramide orogeny. Quartz-sericite-pyrite+/-chalcopyrite stockwork mineralization exhibits uniform northeast to east-northeast strike orientations (Preece, 1986).
Mid-Tertiary, and Basin and Range Structures

A series of northwest-striking normal faults cut the Laramide-age structures in the district as a result of mid-Tertiary extension and regional tectonism from the late Oligocene through the late Miocene (Walker, 1995). The Eagle Creek fault bounds the Morenci district along the southwestern margin and offsets Paleozoic through Cretaceous sedimentary rocks and Laramide-age intrusive rocks against over 1,160 m (3,800 ft) of basin fill and mid-Tertiary volcanic rocks (Figure 23). The Apache, Copper Mountain, Kingbolt, and North faults in the mine area are parallel to the Eagle Creek fault and record structural dislocations between 60 and 240 meters (200 and 790 ft) (Figures 30 and 31). Drill hole evidence shows that monzonite porphyry intruded the Kingbolt fault during Laramide-time as well as movement during the mid-Tertiary. The Copper Mountain fault offsets the supergene enrichment blanket in the Morenci area (Lindgren, 1905a), and the timing of enrichment (see Geochronology chapter) indicates that at least some of the northwest-striking faults were reactivated or continued to be active during subsequent Basin and Range normal faulting.

A series of northeast-striking and north-south-striking normal faults cut the older structures in the district as a result of re-activation of older faults and continued deformation during mid-Tertiary extension and Basin and Range tectonism. The San Francisco fault bounds the Morenci district along the southeastern margin and offsets Paleozoic through Cretaceous sedimentary rocks and Laramide-age intrusive rocks against over 915 m (3,000 ft) of basin fill and mid-Tertiary volcanic rocks (Figure 24). The Las
Terrazas, Chase Creek, El Paso, West, War Eagle, and related faults record concurrent normal faulting in the mine area (Figure 10).

Post-Laramide, normal faulting in the Morenci district ultimately resulted in the axial Chase Creek graben (Figure 10). The principal fault systems include: 1) the northeast-dipping Copper Mountain and southwest-dipping Kingbolt faults in the Morenci area, 2) the east-dipping Las Terrazas and west-dipping War Eagle faults in the Metcalf and Northwest Extension areas, and 3) the east-dipping Chase Creek and west-dipping El Paso and North faults in the Garfield and Shannon areas. This system of faults created the axial graben in the center of the Morenci district that hosts the thick, high-grade supergene enrichment blanket (see following chapter).

**Hydrothermal Alteration and Mineralization**

Because of the intense textural destruction that accompanied pervasive hydrothermal phyllic and supergene argillic alteration, the study of hydrothermal alteration has been difficult. This has required detailed and time-consuming examination of outcrops, core, and thin and polished sections from samples collected during routine mapping and core logging. Langton, Bennett and Schern (Phelps Dodge, 1978) produced a generalized alteration map for the district based on drill holes and mapping (Figure 27). Preece (1986) and Preece, Stegen and Weiskopf (1993) described the hydrothermal alteration and mineralization at Morenci in terms of cross-cutting vein assemblages. This work was based on field and laboratory studies including reconnaissance fluid inclusion measurements, and established the current basis for classifying alteration and hypogene
mineralization. Calkins (1997) used petrographic study, X-ray diffraction, X-ray florescence, and stable isotopes of oxygen and hydrogen to characterize hypogene and supergene phyllosilicate minerals. Most recently, Holick (1998) completed a fluid inclusion study of samples from across the district along with gas chromatography and bulk leachate analyses to determine hydrothermal fluid geochemistry. The distributions of hypogene copper and molybdenum mineralization are shown in Figures 33 and 34, respectively, based on the Morenci drill hole database discussed in the following chapter. For earlier, detailed descriptions see Lindgren (1905a), Reber (1916), and Moolick and Durek (1966). Fluid inclusion data and vein characteristics are summarized in Table 10. Characteristic alteration styles are briefly noted with the unit descriptions above.

The descriptions below follow the classification scheme of Preece (1986) and have been summarized from Preece, Stegen and Weiskopf (1993) along with supplemental data from the other studies mentioned above. This work showed that temporal variations of intrusion-hosted vein assemblages are essentially identical district-wide, and a systematic progression of fluid characteristics occurred through time. From oldest to youngest, this paragenetic sequence consists of 1) early veins of biotite+ magnetite, quartz+ feldspar, and quartz+ molybdenite, 2) main-stage veins of quartz+ sericite+ pyrite +/- chalcopyrite, and 3) late fissure veins of relatively high-grade Cu-Zn-Au-Ag mineralization with manganese, quartz and pyrite. The alteration zones as shown on Figure 27 are defined by a combination of selective vein and pervasive alteration. Where selective vein alteration predominates, the zone is defined by the presence of the most abundant vein type.
Where alteration affects large masses of rock, the zone is defined by the mineralogy of the pervasive alteration.

**Early Veins**

**Character:** The earliest veins, defined here as the potassic association, are generally composed of quartz +/- orthoclase +/- chalcopyrite, but also include biotite + magnetite veins that occur in a broad aureole around the district. In the more mafic Precambrian and Laramide intrusive host rocks, biotite + magnetite veins precede the quartz +/- orthoclase veins; however, in the Morenci and Garfield areas, massive biotite veins have been observed to cut early quartz +/- orthoclase veins (Parker, pers. commun.). Where present, early quartz + molybdenite veins cut the potassic veins. Sphene, rutile and apatite are common accessory minerals. Carbonates are present in some of the quartz + orthoclase veins from deep drill holes. The early veins typically exhibit variable vein orientations compared to later-stage veins (Preece, 1986).

**Distribution:** The early veins are generally restricted to the Monzonite and Older Granite Porphyries (Figures 28 and 33). However, magnetite +/- biotite veins occur at depth and in outlying areas up to 2 km from the center of the district. Quartz + orthoclase \((K_1)\) veins and K-feldspar flooding of the groundmass occur at depth in drill holes in the Garfield, Coronado, and Western Copper areas. Because of intense supergene alteration, quartz-orthoclase veins are typically recognized deep in the system and are only rarely found in the upper levels of the deposit where they have been overprinted by supergene alteration. Quartz + molybdenite veins appear to have been deposited in both monzonite
porphyry and older granite porphyry principally along the margins of the older granite porphyry intrusive complex (Figures 28 and 34). Average molybdenum grades are low (0.010% Mo) with the highest grades in the Western Copper, Northwest Extension, Coronado, and Metcalf areas. McCandless and Ruiz (1993) reported a Re-Os date on a sample of molybdenite from Metcalf of 54.9 +/- 0.9 Ma (revised, Table 3).

Fluid inclusion data: Fluid inclusion studies show that the paragenetically early quartz + orthoclase veins are the highest temperature assemblage veins measured in the district (Preece, 1986). Early quartz + orthoclase veins contain halite-bearing fluid inclusions that homogenized by vapor disappearance at 250-310°C and contained salinities of 30-35 wt.% NaCl equiv. Later quartz + orthoclase veins contained halite-bearing inclusions that homogenized at 320-360°C and contained salinities of 39-43 wt.% NaCl equiv. Co-existing liquid- and vapor-rich, two-phase inclusions indicate low-salinity fluids that boiled at 375°C and at 400-450°C at pressures of 210 and 260-360 bars, respectively (Preece, Stegen and Weiskopf, 1993).

Fluid inclusion studies (Preece, 1986) show that the early quartz + molybdenite veins contain inclusions that are similar to those observed in the late quartz + orthoclase veins. The quartz + molybdenite veins contain predominantly low-salinity (2-10 wt.% NaCl equiv.), liquid-rich inclusions that homogenized at 310-400°C, and one high salinity (41 wt.% NaCl equiv.) inclusion that homogenized by halite dissolution at 340°C.
Main-stage Veins

Character: The main stage of mineralization consists of multiple generations of cross cutting quartz + sericite +/- pyrite +/- chalcopyrite veins and veinlets that form a stockwork with fracture densities ranging from 0.1 to over 1.0/cm. This assemblage also includes barren quartz veins which cut and are cut by quartz + sericite + pyrite veins. In some areas, minor later quartz + molybdenum veins appear to be contemporaneous with the main stage assemblage (Preece, 1981). Veins are generally less than 5 mm thick, and consist predominantly of pyrite and subordinate quartz. Vein controlled halos, typically 5 to 20 mm wide, are composed of felted mats of quartz + sericite + pyrite that obliterate primary textures. Pyrite + chalcopyrite-bearing micro-fractures without silicate alteration halos commonly occur and cut the larger sericite-bearing veins. Chalcopyrite +/- minor inclusions of pyrrhotite +/- sphalerite occur as blebs in pyrite and as discrete grains in veins and haloes. Lindgren (1905a) and Moolick and Durek (1966) reported that zinc, as sphalerite or zinc blende, occurs in concentrations in the protore only slightly less than copper. Preece (1981) reported that magnetite appears to replace chalcopyrite in some veins, and Parker (pers. commun.) observed magnetite replacing steel-glance chalcocite in other veins in the deeper high-grade hypogene zone below the Morenci pit. Interestingly, North (pers. commun.) observed massive magnetite veins with sericite selvages at Coronado.

Distribution: Quartz + sericite + pyrite +/- chalcopyrite veins are associated with intense quartz-sericite-pyrite alteration of the wall rocks and more uniform northeast- to east-northeast-striking orientations. In some areas of the district, this is the only vein
assemblage present. Quartz-sericite in the veins can be distinguished from the wall rock particularly in older granite porphyry where they occur as grey selvages along the veins in an otherwise whitish rock. In monzonite porphyry, however, the quartz-sericite veins are more difficult to distinguish from the pervasively quartz-sericite altered groundmass.

Figure 27 shows three styles of quartz-sericite-pyrite alteration, the boundaries of which are usually gradational. Intense QSP$_3$ alteration typically accompanies the quartz monzonite porphyry stocks and completely obliterates the original texture of the rock in places. Moderate QSP$_2$ alteration typically occurs in and adjacent to the older granite porphyry as a stockwork of veins with 1 to 2-cm (0.4 to 0.8 in) wide grey sericite selvages and partially altered feldspar phenocrysts and groundmass in the intervening wall rock. Weak QSP$_1$ alteration occurs in areas of the district where the vein density is typically less than 0.2/cm such as in the younger granite porphyry complex and outlying Proterozoic granite country rock. In these areas, quartz-sericite-pyrite alteration ranges widely in character as a function of fracture density and usually follows structures and porphyry dikes. Weak QSP$_1$ alteration is typically selective and restricted to veins with the intervening country rocks typically weakly altered to fresh-appearing.

Quartz + sericite + pyrite +/- chalcopyrite veins occur in spatially distinct domains. The pyrite-rich assemblage typically occurs higher in the system and peripheral to the center of the district, and the chalcopyrite-rich assemblage typically occurs deeper in the system and focussed on the central intrusive complex (Figures 28 and 29). The average total sulfide content in hypogene mineralization is slightly over 3 wt.% and ranges from <0.03 to over 20 wt.% pyrite + chalcopyrite. The highest sulfide contents (>4 wt.% py +
Chalcopyrite-rich quartz + sericite veins occur along the southeast side of the deposit. Chalcopyrite averages 0.56 wt.% and ranges from 0.025 to over 2.9 wt.% and correlates directly with the distribution of hypogene copper grade in Figure 33. Pyrite averages 2.5 wt. % and ranges from 0.012 to over 18 wt.%. Although the average copper grade in the hypogene zone is 0.16% Cu, there are some parts of the deposit with average grades of 0.43% Cu as chalcopyrite. Except for those high-grade hypogene zones, much of the deposit classified as hypogene in character exhibits a weak supergene overprint; thus, the actual primary copper grade in the deposit was probably lower than 0.16% Cu (see following chapter).

Chalcopyrite-rich quartz + sericite veins occur in continuous higher-grade zones (>0.30% Cu) around the district. The volumetrically largest of these occurs along the southeastern contact of the monzonite porphyry stock in between the hanging wall of the Kingbolt fault and footwall of the Quartzite fault (Figures 28 and 33). These veins are typically 5 to 10 mm thick and contain quartz +/- chalcopyrite +/-magnetite and cross cut earlier potassic and molybdenite veins. Typically, the pyrite-to-chalcopyrite ratio is <1.

Fluid inclusion data: Fluid inclusion studies (Preece, 1986) show that quartz + sericite + pyrite veins contain two-phase inclusions that homogenize at slightly lower temperatures (290-360°C) and with higher salinities (5-15 wt.% NaCl equiv.) than inclusions in the quartz + molybdenite veins. A single pair of liquid-rich and vapor-rich inclusions provided limited evidence of boiling. These inclusions homogenized at 354°C and indicated a pressure of 160 bars. Preece, Stegen and Weiskopf (1993) reported similar temperatures (330-370°C, T_b) and salinities (5-8 wt.% NaCl equiv.) for primary inclusions in the quartz + sericite + chalcopyrite veins. They also noted that a few
inclusions contained chalcopyrite and sylvite daughter minerals, which they interpreted to be possibly formed from distinctly different fluids.

**Late Fissure Veins**

**Character:** Large, continuous quartz + sulfide fissure-veins represent the latest hydrothermal event in the district. Vein widths are 10 cm (4 in) to over 1 m (3 ft). Individual veins strike on the order of hundreds of meters and exhibit district-wide northeast strike directions. Preece, Stegen and Weiskopf (1993) reported that geochemical analyses and polished section microscopy indicate that these veins contain relatively high-grade Cu-Zn-Au-Ag mineralization in a matrix of ubiquitous quartz and pyrite. In addition, late fluorite veins that contain euhedral chalcopyrite crystals cut late quartz and barren pyrite veins at Garfield (Parker, pers. commun.). The ages of the late fissure veins have not been determined, and they could represent either a late Laramide event, or a mid-Tertiary overprint.

**Distribution:** Late fissure-veins are distributed throughout the Morenci district. Manganese-silver veins are common in the Paleozoic limestones up to 10 km (6 mi) away from the center of the district, and form much of the mineralization in the Copperplate Gulch area (Plate 1). Gold occurs in the Garfield fault, and is generally richer in the less altered margins of the deposit and in the peripheral veins to the northeast and southwest of the district (Lindgren, 1905a; Moolick and Durek, 1966).

**Fluid inclusion data:** Preece (1986) reported the results of a study that traversed across a 3-m wide quartz + calcite vein in silicified Ordovician Longfellow limestone.
The vein is located about 2 km south of the Morenci pit and contains local silver with minor gold mineralization associated with variable amounts of manganese oxides and Cu-Zn-Pb sulfides. Fluid inclusion and petrographic studies indicated that, with time, the fluids responsible for quartz deposition cooled from 330°C to 250°C and became more dilute from 6 to 3 wt.% NaCl equiv. He further noted that the earliest inclusions (330°C, 6 wt.%) in the quartz + Ag + Mn vein overlapped the temperature and salinity of the fluid inclusions in the stockwork quartz + sericite + pyrite +/- chalcopyrite veins. Preece (1986) documented boiling at 300-310°C and at 260-280°C that corresponded to pressures of 100 and 40 bars, respectively. These pressures lead to the interpretation that they may have been emplaced at shallower levels below the surface and beg the question of whether the late fissure veins are indeed mid-Tertiary instead of Laramide in age.

Skarns

**Character**: Calc-silicate alteration and associated Cu-Zn sulfide +/- magnetite mineralization occur in skarn zones in Paleozoic limestones and shales around the district (Figure 27). This style of sulfide mineralization is predominantly vein-controlled and occurs adjacent to the monzonite and older granite porphyry stocks and dikes with only minor local massive replacement bodies. Although volumetrically small, the Paleozoic section hosts some of the higher-grade mineralization and much of the oxide mineralization in the district. Early underground production targeted the high-grade supergene mineralization in these zones.
Calc-silicate alteration and mineralization occurred in two principal stages (Bennett, 1974; Preece, Stegen and Weiskopf, 1993) that correspond with the alteration and mineralization in the adjacent intrusive rocks. The early anhydrous stage is marked by trace amounts of sulfides and magnetite with diopside in the shales and with andradite garnet in the limestones. The later hydrous stage formed veinlet-controlled and massive assemblages of actinolite, tremolite, chlorite, epidote, and calcite from the early-stage anhydrous minerals. Pyrite, chalcopyrite and magnetite, and accessory sphalerite and bornite occur in veinlets generally associated with the hydrous assemblage. Magnetite forms locally extensive, large replacement bodies in limestone in contact with dikes. Skarn alteration affects each unit differently depending on host-rock lithology, and these characteristics are briefly noted in the unit descriptions in the Stratigraphy section above.

**Distribution:** Sedimentary rock-hosted mineralization occurs in all of the Paleozoic formations. Although locally the Coronado Quartzite contained some of the highest grades in the district, the total copper and oxide copper contents generally diminish with depth in the Paleozoic section. The bulk of the mineralization in the Paleozoic rocks occurs in the Southside and Shannon areas of the district, and in smaller zones in the Garfield area (Figure 29, see also Lindgren, 1905a).

Peripheral Zone

Alteration and mineralization in the periphery of the Morenci district has not been well characterized, even today. The generalized alteration map shown in Figure 27 is based on drill holes and mapping from Langton, Bennett and Schern (Phelps Dodge, 1978)
and displays a bias towards the classic Lowell and Gilbert model (Lowell and Guilbert, 1970) that was in vogue at the time. Recent mapping in the district, however, has not substantiated the model. Although chlorite + epidote alteration occur in some areas of the district, the map portrays a “propylitic” halo that is not present in such a widespread area.

Hydrothermal alteration occurs in some peripheral areas of the district. Chlorite + epidote alteration of rock-forming minerals occurs in the southwest quadrant of the district where it occurs in diorite and monzonite porphyry dikes and as hornfels alteration in Pinkard Formation. In other areas of the district adjacent to the main mineralized area, particularly in the northwest quadrant, shreddy, secondary biotite that is partly altered to chlorite is present in Proterozoic granite. The periphery of the district also contains structurally controlled quartz-sericite-pyrite alteration, as described above, and local zones with magnetite +/- biotite veins. Towards the edges of the district on both the Eagle Creek and San Francisco sides, specular hematite +/- quartz, and earthy hematite + goethite, presumably after sulfides, occur as 0.5 to 1 mm wide veins with fracture densities from 0.05 to 0.1/cm. In some locations, 1 mm wide goethite + earthy hematite veins contain biotite selvages up to 5 cm wide. Small monzonite porphyry intrusions and dikes throughout the district contain variable amounts of quartz + sericite +/- pyrite.
DISTRIBUTION AND CHARACTER OF SUPERGENE ENRICHMENT IN THE MORENCI PORPHYRY COPPER DEPOSIT

Introduction

The Morenci district covers over 90 km² (35 mi²) and contains a mineralized area that occupies at least 19 km² (7.5 mi²) (Figure 33). Over the years, the tug of war between exploration and mining operations has necessitated a focus on individual mineralized areas of the district, a function of economics rather than geology. This has ultimately resulted in a large database of drill holes and mapping that can now be used to evaluate the distribution and character of mineralization at a district scale. Although the focus of this study is on supergene mineralization, additional information about the hypogene zone was discovered during this study and is included in appropriate sections of this chapter as it relates to the supergene system.

This study was a collaborative effort between the Geology Department at Phelps Dodge Morenci, Inc. and the Department of Geosciences at the University of Arizona. The work primarily involved the construction of a representative, district-wide geologic database from drill holes and surface mapping at scales from 1:6,000 to 1:2,400. This research database was used to map and evaluate selected geologic characteristics of the Morenci deposit at a district scale. These studies provided constraints for a simple, first-order, three-dimensional mathematical model based on mass balance principles to de-enrich the deposit and look at district-scale enrichment characteristics, eroded thicknesses, and pre-enrichment paleo-topography. In addition, the interpretations of supergene mineral profiles were based on two cross sections and one long section across the district,
evaluations of the Morenci, Metcalf, and Northwest Extension areas, detailed mineralogical profiles from selected core holes, and polished thin section and electron microprobe study of selected samples. Table 11 contains a list of the common supergene minerals at Morenci and their chemical formulas for reference.

Database Evaluation and Mapping

Method of Study

The Morenci drill hole database is a rich source of geologic information that was used to evaluate the distribution and character of a variety of geologic parameters throughout the district. This work was conducted in three phases. The first phase was an orientation study of the Garfield area, where mapping is of good quality (Pawlowski et al., 1997), and the drill holes are recent, well distributed and well logged. Trial plots of copper grade, zone thickness, and copper grade x thickness were developed. Based on those results, the study was expanded to include the entire district for the second phase of work. The original results for the entire district showed that a few areas required supplemental information, which was included in the third phase of work.

The basic approach was to build a subset of the Morenci drill hole database that represented the district. The data were composited into four mineralogical zones. Selected geologic parameters were then modeled for each zone and plotted for subsequent evaluation. These parameters were then used to develop a simple, first-order mathematical de-enrichment model of the district based on mass balance principles. The
procedures, results, and geologic interpretations are described in more detail in the following sections.

Database

Drill hole selection: At the time of this study, the Morenci database consisted of 47,927 samples from 3,079 core, reverse circulation, and churn holes that were drilled between 1915 and mid-1998 (Figure 35). Drill hole spacing is highly variable and ranges from 30 m (100 ft) or less to over 500 m (1,600 ft) in places. Because many different drilling programs were conducted over the last 85 years in an active mine setting, many drill holes penetrated only a small portion of the deposit. To create a useful database for a district-scale evaluation and subsequent mass balance calculations, the Morenci staff were asked to choose representative drill holes from their project areas that met specific criteria. The holes were no closer together than about 122 m (400 ft), and they must have been collared at or above the pre-mine topographic surface (e.g. in stockpiles), penetrated the entire supergene zone, and bottomed in hypogene mineralization at total depth.

For the research data set, 759 holes or about 25% of the drill hole database were selected to represent the deposit on a district scale (Figure 35). A total of 722 holes were chosen during the first phase of work. Of these, 19 holes were “spliced” together from two or more drill holes at the same location, but penetrating different elevations to generate a complete profile. Another 37 drill holes were added to the database for the third phase of work to fill in the Coronado, Western Copper, and Shannon areas.
Data distribution: In some areas, the resulting drill hole distribution is still not very uniform (Figure 35). In particular, the northwestern quadrant of the district centered on the Candelaria breccia and younger granite porphyry complex is sparsely drilled due to stockpile cover. In addition, the important central portion of the Morenci pit in the Copper Mountain area has many holes, but almost all are short, or do not penetrate enough of the deposit to be useful. The outline of the mine plan basically conforms to the outer limits of the drill hole pattern, and indicates that the deposit is open-ended in several directions and is not entirely represented in the database. The overall distribution, nonetheless, provides a fairly good three-dimensional representation of the well-mineralized portion of the Morenci district.

Quality and data type: The quality of the geologic logs is highly variable. Because of the selection criteria, many of the holes are from the more recent drilling programs that started in the mid-1980’s, were drilled deeper, and have well documented geologic logs. In general, all of the geologic logs record some type of data on lithology, alteration, and mineralogy. Some of this information has been historically captured in the database and includes: % Cu (total), %XCu (acid-soluble copper, leach extraction), %MLT (1-hour, ambient temperature, ferric-soluble copper, leach extraction), % Mo, oz/t Au, oz/t Ag, %Fe, %S, rock-type codes, sulfide mineral codes, oxide mineral codes, covellite codes, zone codes (structural or lithological domain), and population codes. The Morenci database design has been modified numerous times, and a large number of older holes have been re-logged as part of various projects over the last 10 years. Unfortunately, alteration was not included until very recently and was not available except on the written logs.
Population Codes and Mineral Zones

As part of routine geology operations, the Morenci staff has devised population codes to identify broad zones that have undergone similar physicochemical leaching and enrichment processes (Parker, 1998). These codes are useful in defining large-scale features associated with the supergene and hypogene zone across the Morenci district, and are based in part on economic as well as geologic criteria. Detailed mineral profiles generated from hand specimen observations combined with analytical data are required, however, to evaluate the local geologic environment. The Morenci population codes represent copper and iron-bearing mineral assemblages and textures common to a particular geologic environment. Summary statistics of the associated mineralized zones are shown in Table 12 and a typical profile is shown in Figure 6. The descriptions of these populations below are based on Phelps Dodge (1998) and were carried over to the research database.

Population 1 – leached capping: This population represents leached capping typically at the top of the supergene profile and structurally controlled zones of leaching that penetrate the enriched blanket below. Rocks in this zone show physical evidence of leaching of the original sulfide minerals. This evidence includes the presence of hematite, goethite, or jarosite as products from the dissolution of vein or disseminated pyrite, chalcocite, and chalcopyrite. This can include classic boxwork or transported iron oxide textures (Blanchard, 1968). Copper may occur as neotocite, tenorite, cuprite, or native copper; however, copper content is generally less than 0.10% Cu and shows little
continuity across the zone. The boundary with the enriched blanket is generally very sharp, typically less than 10 m (30 ft). Across the district, the leached capping averages 82 m (269 ft) thick and 0.07% Cu.

Population 2- partially leached: This population represents in-situ oxidation or partial leaching of sulfide minerals in an earlier-cycle enrichment blanket. Rocks in this zone may contain brochantite, malachite, azurite, chrysocolla, tenorite, and copper wad in totally oxidized areas. Oxide mineralization typically exhibits good continuity and average copper grades are locally as high as in the enriched blanket. Rocks of population 2 may also include pyrite, chalcocite, and chalcopyrite without copper oxides typical of the enriched blanket. The bulk continuity and grade of copper mineralization where sulfides remain, however, have been diminished due to leaching along fractures and at the top of the enriched blanket. The ferric soluble copper (%MLT) values average 56%, but are highly variable and depend on the relative proportions of the different copper minerals present at any particular location. Across the district, the zone of partial leaching averages 99 m (325 ft) thick and 0.28% Cu.

Population 3 – enriched blanket: This population represents the composite supergene enriched blanket. Rocks in the enriched blanket contain significant amounts of supergene chalcocite, djurleite, digenite, and covellite along with variable amounts of relict pyrite and chalcopyrite. Continuity of mineralization is generally excellent, and the average copper content is typically two to five times the local hypogene grade below, derived dominantly from the supergene sulfides. Transported iron oxides may be present along fractures, but the oxide copper content of this zone is typically less than 5 wt.% of
the total copper content. A composite profile results from downward zoning in the enriched blanket typically from a chalcocite >> covellite + chalcopyrite assemblage at the top of the blanket to a chalcopyrite + covellite > chalcocite assemblage at the base. Because each copper sulfide mineral has a different solubility, the ferric soluble copper (%MLT) values are therefore highly variable and depend on the relative proportions of the different sulfide minerals present at any particular location. These values average 35% and can range from highs 51% of the total copper content in chalcocite-dominant assemblages, to as low as 10% in chalcopyrite-dominant assemblages. Values greater than 55% may occur in small partially leached areas as in Population 2. Across the district, the enriched blanket averages 130 m (427 ft) thick and 0.47% Cu.

Population 4 - hypogene: Although this population represents the primary, low-grade protore mineralization, supergene effects may still be present in some areas. Rocks in the hypogene zone typically contain un-enriched pyrite and chalcopyrite with minor amounts of bornite, and variable amounts of magnetite. Trace amounts of chalcocite and covellite may be found in the zone to considerable depths, but their contribution to the total copper content is generally low. Ferric soluble copper contents average only 21% of the total copper content and oxide copper contents are typically not detectable (<0.01% Cu). Across the district, the low-grade hypogene mineralization has an unknown depth and averages 0.16% Cu.

Population 5 – high-grade hypogene: This population represents about 10% of the total known hypogene mineralization and is associated with coherent volumes of rock with copper contents typically >0.30% Cu, predominantly as chalcopyrite, and with bornite in
the Garfield and Morenci areas. The bulk of this material occurs at depth in the Morenci pit area in between the Kingbolt and Quartzite faults and averages 0.43% Cu. Supergene processes have typically not affected these zones, and this is reflected in the low average ferric soluble content of only 9%. Typically population 4 and 5 are grouped together and their combined copper content averages 0.19% Cu.

Estimation of Sulfide Mineral Abundance and Ratios

Because of contrasting logging practices over the last 85 years, this has made it difficult to correlate estimates of mineral abundance from geologist to geologist, program to program, area to area, and hole to hole. Analytical data for copper, iron, and sulfur however, are reliable and available from many of the drill holes. This permits estimation of pyrite, chalcopyrite, and chalcocite contents and ratios from the analytical data, given certain simplifying assumptions.

Methods: Pyrite contents can be estimated from analytical data, if the weight % copper and sulfur contents are known. The underlying assumptions in the hypogene zone include: 1) all of the non-oxide copper is tied up in chalcopyrite, 2) the other copper sulfide minerals are insignificant, 3) any remaining sulfur not attributed to chalcopyrite is tied up in pyrite, and 4) there is excess iron to satisfy all other mineral phases. The basic mass balance statement is that the excess sulfur content available for pyrite equals the total sulfur content of the sample less the sulfur content in chalcopyrite. Equation (1) shows this relationship, solving for wt.% pyrite:
(1) \[ \text{wt\% py} = \left[ \% S_{\text{total}} - \left( \frac{\text{TCu} - \text{XCu}}{\text{Frac Cu}_{\text{cpy}}} \right) \times \text{Frac S}_{\text{cpy}} \right] / \text{Frac S}_{\text{py}}, \] where

\( \text{TCu} = \) wt. % total copper from analysis
\( \text{XCu} = \) wt. % oxide copper from analysis
\( \text{Frac Cu}_{\text{cpy}} = \) fraction of copper in chalcopyrite = 0.346
\( \text{Frac S}_{\text{cpy}} = \) fraction of sulfur in chalcopyrite = 0.349
\( \text{Frac S}_{\text{py}} = \) fraction of sulfur in pyrite = 0.535

By the same reasoning, pyrite contents can be estimated for the enriched blanket if parallel assumptions are made: The underlying assumptions in the supergene blanket include: 1) all of the non-oxide copper is tied up in chalcocite and the other copper sulfide minerals are insignificant, 2) any remaining sulfur not attributed to chalcocite is tied up in pyrite, and 3) there is excess iron to satisfy all other mineral phases. The basic mass balance statement is that the excess sulfur content available for pyrite equals the total sulfur content of the sample less the sulfur content in chalcocite. Equation (2) shows this relationship, solving for wt. % pyrite:

(2) \[ \text{wt\% py} = \left[ \% S_{\text{total}} - \left( \frac{\text{TCu} - \text{XCu}}{\text{Frac Cu}_{\text{cc}}} \right) \times \text{Frac S}_{\text{cc}} \right] / \text{Frac S}_{\text{py}}, \] where

\( \text{Frac Cu}_{\text{cc}} = \) fraction of copper in chalcocite = 0.799
\( \text{Frac S}_{\text{cc}} = \) fraction of sulfur in chalcocite = 0.201

The chalcopyrite content in the hypogene zone can be estimated directly from analytical data using the wt. % copper content. The only requirement is to assume that
chalcopyrite is the only copper-bearing mineral phase. Equation (3) shows the relationship in that case. Given the wt. % pyrite and chalcopyrite contents, the py/cpy ratio can then be easily calculated.

\[
\text{(3)} \quad \text{wt}\% \text{ cpy} = \frac{(T\text{Cu} - X\text{Cu})}{\text{Frac Cu}_{\text{cpy}}}. 
\]

Similarly, the chalcocite content in the enriched blanket can be estimated directly from analytical data using a parallel assumption. In this case, we have to make the rather dubious assumption that all of the copper is tied up in chalcocite, and that the other sulfide minerals like covellite and chalcopyrite are insignificant in abundance. Equation (4) shows the relationship in that case. Given the wt. % pyrite and chalcocite contents, the py/cc ratio can then be easily calculated.

\[
\text{(4)} \quad \text{wt}\% \text{ cc} = \frac{(T\text{Cu} - X\text{Cu})}{\text{Frac Cu}_{\text{cc}}}. 
\]

Enrichment factors relate the copper content in the enriched blanket to the underlying hypogene mineralization and reflect the net amount of upgrading resulting from supergene enrichment processes. These are reported as ratios and simply calculated by dividing the copper grade in the enriched blanket by the local hypogene grade below as shown in equation (5). An enrichment factor >1 indicates that copper has been added to the enriched zone by replacement of chalcopyrite and pyrite with chalcocite or other secondary sulfide minerals. An enrichment factor of 1 indicates that the grade of the
blanket is the same as the underlying primary hypogene mineralization. In this case, supergene processes resulted in a change in mineralogy, but without an increase in copper content. An enrichment factor <1 indicates that copper has been locally removed from the enriched zone by subsequent leaching.

\[
(5) \quad EF = \frac{TCu_{\text{pop 3}}}{TCu_{\text{pop 4,5}}} \quad \text{where:}
\]

- \( EF \) = enrichment factor
- \( TCu_{\text{pop 3}} \) = average copper grade in the enriched blanket
- \( TCu_{\text{pop 4,5}} \) = average copper grade in the hypogene zone

**Error Analysis:** The assumption that chalcocite is the only copper-bearing mineral in enriched blanket is the most tenuous assumption of the group. By definition, the hypogene zone contains only pyrite and chalcopyrite, with very minor bornite; however, the ferric soluble values indicate that minor amounts of chalcocite and covellite are present. In this zone, the most significant assumption is the distribution of iron among the minerals. For the purposes of this simple exercise, iron content was not used as a further constraint. We do know that chalcocite is not the only copper-bearing mineral, however, in the enriched blanket. In reality, the excess sulfur content available for pyrite is equal to the total sulfur content less the sulfur content in chalcocite, covellite, and chalcopyrite. The error in estimating pyrite content associated with the assumption that all of the copper is chalcocite is small if the sulfur to total copper ratio is high (Griffin, 1997). The error increases with decreasing sulfur content and increasing covellite or chalcopyrite content.
(Figure 36). Given relative proportions of chalcocite, covellite, and chalcopyrite from logging, the estimates can be significantly improved, but these data are not uniformly available across the district. As a result, interpretation of chalcocite abundance and pyrite to chalcocite ratios needs to be done with appropriate caution.

De-enrichment and Reconstruction

The 759-hole district database was used to develop a simple, first-order mathematical de-enrichment model of the district based on mass balance principles. The de-enrichment model was based on one-dimensional mass balance calculations for each drill hole in the district database. These data were then modeled in two dimensions as described in the section below, thus providing a three-dimensional representation of the eroded thicknesses and pre-enrichment paleotopography across the district.

Assumptions: Several important assumptions were made to simplify the calculations. The first assumption is that there is only downward, vertical transport of copper. This is an over simplification in a district like Morenci where lateral migration has been well documented. Nevertheless, it is a reasonable first-order approximation with which to start and is required to keep the problem tractable. The second assumption is that the average copper grade in the hypogene zone at depth is representative of the hypogene mineralization in the entire overlying supergene zone and that no significant vertical zoning was present. The third assumption is that copper is conserved (i.e. chemical weathering is 100% efficient and outpaces erosion so that all of the copper is leached from the overlying rocks, before it was eroded from the deposit). This assumption seems reasonable given the
lack of significant exotic deposits around the district. The fourth assumption is that density
is constant (i.e. bulk density differences due to supergene silicate alteration, porosity
changes, and sulfide mineral content are insignificant at the first order).

**De-enrichment:** The mass balance statement is based on conservation of copper.
That is, copper added to the enriched blanket at depth must equal the amount efficiently
leached from the rocks that have been eroded away and from the remaining leached
capping and partially leached zones below. Equation (6) gives the relationship solving for
the thickness of the eroded column.

\[
(6) \quad Z \cdot G_h = L \cdot (G_l - G_h) + P \cdot (G_p - G_h) + B \cdot (G_b - G_h)
\]

where:

- \( Z \) = the thickness of the eroded column
- \( L \) = the thickness of the remaining leached capping
- \( P \) = the thickness of the partially leached zone
- \( B \) = the thickness of the enriched blanket
- \( G_h \) = the average copper grade in the hypogene zone at depth
- \( G_l \) = the average copper grade in the leached capping
- \( G_p \) = the average copper grade in the partially leached zone
- \( G_b \) = the average copper grade of the enriched blanket

**Paleotopographic reconstruction:** A reconstruction of the pre-enrichment
paleotopography was generated from the calculated eroded thicknesses. This simply
involved adding the calculated eroded thickness to the drill hole collar elevation corrected
for any topographic irregularities such as stockpiles above or excavations below the pre-
mine topographic surface. These data points were then contoured using the method
described below. The resulting representation of the pre-enrichment surface, however, is
only valid for those areas within the influence of the drill holes. Presumably, erosion of
the surrounding terrain proceeded at a similar rate, but this was not accounted for at the
edges of the contours (see results discussed below).

Modeling

A number of characteristic geologic features of the Morenci district were modeled
and mapped from the database. First the database was subdivided into four principal
populations to represent the leached capping, partially leached (enriched blanket),
enriched blanket, and hypogene zones. Because these represent stacked profiles with
different reference elevations, they provide a pseudo-three-dimensional representation of
the Morenci deposit. Variable-length composites that honored population code were
generated for %TCu, zone thickness, and grade-times-thickness for each of the three,
supergene populations. Composite lengths for population 4 and 5 samples are highly
variable and range from 15 to 60 m (50 to 200 ft) to over 300 m (1,000 ft) in places.
Composite values for each population were also generated for rock-type, % Mo, wt.% py,
wt.% cpy, wt.% cc, py/cpy, py/cc, enrichment factor, eroded thickness, and pre-enrichment
surface elevation. Midpoints for the composites of each population were forced to a single
plane and then loaded into the MEDSYSTEM® program for manipulation. Classical
statistics and probability plots were then produced to select meaningful contour values for
data display. MEDSYSTEM® is a software package widely used by geologists, engineers, and technicians for geologic modeling, mine planning, and mine operating design that contains classical statistics and geostatistical programs.

For each chosen parameter, a two-dimensional model was created using a 30-m by 30-m (100-ft by 100-ft) cell size. The composites were then used to interpolate values for all cells using the inverse distance method to the third power, and a search strategy of 300-m by 300-m (1,000-ft by 1,000-ft) with a minimum of two and maximum of 15 composites. Rock density differences were ignored because specific gravity and bulk density measurements at Morenci yield a relatively narrow range of values around 2.52 gm/cm$^3$ for all rock-types except for insignificant volumes of diabase and skarns. The 30-m (100-ft) cell size was chosen to equal one third to one fourth of the drill hole spacing. Search distances were chosen consistent with variography results for copper grade from the Metcalf and Coronado geologic block models (Cheff et al., 1997; Young-Mitchell et al., 1998). Inverse distance to the third power was chosen because it yielded the best-fit match from point validation study.

The cells were computer-contoured and the contours were checked against the composite locations and values. Contour smoothing was not used, but the contours were later checked and smoothed by hand for selected maps. This resulted in removing some small, isolated contours and edge effects due to drill hole spacing limitations. At the district scale the contours were not constrained by structural or rock-type domain
boundaries, although this would probably provide more appropriate local contours at a larger scale.

Results

Maps: The results of this work yielded 1:6,000 scale working maps showing the distribution of various geologic features of the deposit at a district scale. The original working maps are located in the Phelps Dodge Morenci, Inc. Geology Department. Selected maps are included in this report. The distributions of hypogene copper and molybdenum mineralization are shown in Figures 33 and 34. Mineral ratios for py/cpy and py/cc are shown in Figures 37. Grade x thickness maps for each population are shown in Figure 38. Enrichment factors, eroded thickness and pre-enrichment paleotopography are shown along with pre-mine topography and surface drainage in Figure 39. Please note that all of these maps were plotted in English units to be consistent with Morenci convention, which departs from the metric convention used in other figures and elsewhere in this paper.

Statistics: Classical statistics from the 3,079-hole Morenci database were also generated for selected parameters for each population. Table 13a shows the distribution of total copper, oxide copper, ferric soluble copper, molybdenum, gold, and silver for each rock-type for all populations at no copper cutoff grade. Table 13b shows the same parameters at a 0.10% Cu cutoff grade to filter out the influence of barren holes outside of the main mineralized area and low-grade leached capping. This only results in a 25% reduction in the number of samples, including the leached capping, and under-scores the conclusion from the distribution of drill holes in Figure 35 that the deposit is still open-
ended. Table 14 shows the same parameters and weighted averages at no cutoff grade for each mineral population.

Summary statistics for the modeled parameters from the 759-hole research database were also compiled. Table 15 shows the overall results for hypogene mineralization and Table 16 shows the results for the supergene zones. Detailed descriptions and interpretations are discussed below for the hypogene zone and in the following section for the supergene zones.

**Distribution of Hypogene Mineralization**

Taken in context with the character of hydrothermal alteration and mineralization described in the previous chapter, it is possible to examine how the nature of hypogene mineralization affects the supergene systematics in the district. The discussion of the distribution of hypogene mineralization and hydrothermal alteration that follows is based on the results obtained above.

**Host Rocks**

The statistics and spatial distribution of mineralization provide important insights about the Morenci district. Interestingly, Laramide porphyries host only 51% of the mineralization $>0.10\%$ Cu in the district (Table 13b). Most of the remaining mineralization $>0.10\%$ Cu occurs in the Proterozoic granite and granodiorite (37%) of the basement complex. Only 4% of the mineralization occurs in the Paleozoic sedimentary rocks. No significant mineralization occurs in the Pinkard Formation, and only minor
amounts of Laramide diorite porphyry are mineralized on the southwest quadrant of the district.

Average copper content in the host rocks is fairly uniform (0.39% Cu) but shows significant variations by rock-type. Monzonite porphyry is the oldest mineralized intrusion and has the highest average copper content (0.48% Cu) of all the intrusive rocks. Copper contents diminish with decreasing age of intrusion from older granite porphyry (0.39% Cu) to younger granite and rhyolite porphyry (0.29% Cu). This trend is also reflected in the distribution of hypogene mineralization in the intrusive rocks (Table 14) from monzonite porphyry (0.19% Cu) to older granite porphyry (0.14% Cu) and younger granite porphyry (0.12% Cu). Interestingly, the younger granite porphyry and older granite porphyry 2 have similarly low primary copper contents. Overall, Proterozoic granite is one of the poorly mineralized host rocks (0.33% Cu) although it has average hypogene copper contents (0.15% Cu). Proterozoic granodiorite is less abundant but a better host rock for both hypogene (0.26% Cu) and supergene (0.65% Cu) mineralization.

Hypogene mineralization at a concentration of <0.05% Cu is not constrained by the drilling (Figure 33). Higher-grade zones (>0.15% Cu) within the district appear to be aligned along a 030° and 040° trends, which is consistent with Laramide structural fabrics in the district. These higher-grade zones are coincident with the southeastern and northeastern margins of the Morenci intrusive complex and straddle the contact between the intrusive rocks and the Precambrian country rocks. The highest grade hypogene zones (>0.25% Cu) and the bulk of the population 5 composites occur in a 2,300-m long by 300-m wide zone on the southeast side of the monzonite porphyry stock along the contact with
the Paleozoic section and underlying Proterozoic granite and granodiorite complex. Interestingly, over 65% of this mineralization occurs in the Proterozoic wall rocks, with the remainder evenly split between the monzonite porphyry and diabase, and the adjacent Longfellow Formation and Coronado Quartzite (compare Figure 33 with Figure 28).

Although volumetrically small, the Paleozoic section hosts some of the higher-grade chalcocite mineralization and much of the oxide mineralization in the district. This may be due, in part, to the reactivity of the carbonate rocks and the fracturing in the underlying quartzite. Total copper and oxide copper contents diminish with depth in the Paleozoic section from the Modoc limestones (0.69% TCu, 0.39% XCu), to the Morenci shales (0.60% TCu, 0.25% XCu), the Longfellow limestones (0.45% TCu, 0.17% XCu), and the Coronado quartzites (0.42% TCu, 0.05% XCu). The bulk of the mineralization in the Paleozoic rocks occurs in the calc-silicate skarn altered rocks of the Southside and Shannon areas of the district, and in smaller zones in the Garfield area (Figure 11a, see also Lindgren, 1905a).

The remaining rock-types represent a small proportion of the deposit. Overall, breccias of all types account for less than 4% of the total deposit (Table 13b). As a group, breccias contain slightly higher than average copper contents (0.43% Cu). By far, fault breccias are the most common and highest grade of this group. Major veins, although volumetrically insignificant in proportion to stockwork and disseminated mineralization, contain some of the higher average copper grades (1.18 % Cu). These veins, however, represented a significant proportion of the early production from the Morenci district.
(Lindgren, 1905a; Moolick and Durek, 1966), but are under-represented in the database because they had mostly been mined out prior to the drilling.

Hydrothermal Alteration

Hypogene copper grade is generally coincident with the margins of the potassic alteration ($K_2$) zone and overprinting strong ($QSP_3$) quartz-sericite-pyrite alteration and stockwork (compare Figure 29 and 33). Lower-grade mineralization (<0.05% Cu) in the central portion of the district is coincident with the younger granite porphyry complex where fracture densities are significantly less (<0.12/cm) than in other parts of the district. Higher-grade zones in the younger granite porphyry are typically associated with small breccia bodies. As noted above, the high-grade hypogene mineralization is coincident with the southeast margin of the strongly altered monzonite porphyry stock and the adjacent skarns developed in the Paleozoic rocks.

Pyrite-to-Chalcopyrite Ratios

Overall, pyrite-to-chalcopyrite ratios are indicative of the bulk primary metal zoning in the hypogene zone at Morenci, but not the character or individual vein types. The average total sulfide content in hypogene mineralization is slightly over 3 wt.% (Table 15), and the highest sulfide contents (>4 wt.% py+cpy) occur along the southeast side of the deposit. Chalcopyrite averages 0.56 wt.% and ranges from 0.025 to over 2.9 wt.%, and correlates directly with the distribution of hypogene copper grade in Figure 33. Pyrite averages 2.5 wt. % and ranges from 0.012 to over 18 wt.% In general, the highest pyrite
contents occur in a “halo” around the higher-grade chalcopyrite zones at the margins of the deposit where copper as chalcopyrite drops off to <0.05% Cu in weak, structurally controlled quartz-sericite-pyrite zones. The pyrite-to-chalcopyrite ratio, therefore, follows a similar pattern (Figure 37a).

Although data are sparse for the Western Copper, Morenci pit, and northwestern areas of the district, several relationships are nonetheless apparent. Overall, pyrite-to-chalcopyrite ratios average 5.6 to 1, and range from 0.05 to over 38. Zones with ratios >8 to 1 occur along the northeastern side of the Garfield and Metcalf areas, southeastern side of the Morenci and Southside areas, and the southwestern side of the Southside, American Mountain, and Coronado areas of the district. This pattern occurs in areas with 2 to 4 wt. % py and very low copper grades. The > 4 to 1 contours enclose parts of Garfield, the western edge of Coronado, much of Northwest Extension, most of Metcalf, and all of the Morenci, Southside, and American Mountain areas, and may represent a pyritic “shell” around the deposit. Zones with ratios <2 to 1 occur in the central parts of the district especially in the Garfield, Coronado, Northwest Extension, inner Metcalf, and Western Copper areas typically associated with the central intrusive complex and attendant potassic alteration (Figures 28, 29, and 37a). Pyrite-to-chalcopyrite ratios exert a strong control on supergene enrichment (Titley and Marozas, 1995). This is very apparent at Morenci as described in the supergene section in a subsequent section.
Molybdenum

The numbers of samples with associated molybdenum analyses are much smaller than for copper, but still provide important information. Only 69% of the samples >0.10% Cu have associated molybdenum assays. Average molybdenum assays (Table 13b) are low (0.010% Mo) and generally reflect the same trends noted for copper relative to rock-type. The distribution of molybdenum in each mineralized zone is shown in Figure 34. In general, molybdenum appears to have been deposited principally along the margins of the older granite porphyry intrusive complex, and has the highest grades in the Western Copper, Northwest Extension, Coronado, Garfield, and Metcalf areas.

Molybdenum mobility in the supergene environment does not appear to be extreme; therefore its distribution can be used to look at hypogene zoning in the overlying supergene environment. Although there is evidence that molybdenum enrichment may occur in some districts, this would require a more alkaline environment in the zone of oxidation, low total sulfide contents (1-2 vol.%), and py/cpy ratios around 1 (Dunn, 1982). At Morenci, this environment appears to be limited spatially. In fact, the distribution of molybdenum is spatially coincident in the enriched blanket, partially leached zone, and leached capping at Morenci (Figure 34), given data distribution limitations. Molybdenum content is slightly higher in the enriched blanket (0.010% Mo) than in the other mineralized zones; but overall, molybdenum grades reflect hypogene values. Preece (1981) noted similar overall molybdenum grades and a relatively sharp local increase at the base of the enriched blanket or roughly the 1,280-m elevation in the Morenci pit.
Molybdenum in the partially leached zone and leached capping is under-represented in the database, but where present, shows a similar distribution pattern to the enriched blanket and underlying hypogene zone. Data for molybdenum are sparse in the partially leached and leached capping due, in part, to sampling protocols that excluded samples from these lower copper grade zones for analysis. Except in the Metcalf and Western Copper areas, molybdenite in the partially leached and leached capping zones has not been mapped or identified in the drill logs. Molybdenite may be oxidized in the weathering process at alkaline pHe and it may concentrate as unrecognized or unrecorded ferrimolybdite (Titley and Enders, 1997). Preece (1981) also reported the iron-molybdenum mineral akaganeite at Morenci. Akaganeite (β-goethite + Mo) has been identified in the Questa porphyry molybdenum deposit in New Mexico (Carpenter, 1968). Experimental work indicates that molybdenite is insoluble at pHe less than 6, which indicates that leaching and enrichment is likely very limited in the typical supergene environment (Carpenter, 1968; Titley, 1963). It is possible that molybdenum occurs as akaganeite and ferrimolybdite and has been overlooked because of the abundance of jarosite, goethite, and hematite in the leached zones at Morenci. It is also possible that molybdenum in the partially leached zone and leached capping has been depleted, and that the overall molybdenum content in these zones is not fairly represented in the database. Thus, there are limitations on interpreting the significance of molybdenum zoning; but in general, the hypogene patterns appear to be reflected in the overlying supergene zones.

Gold and Silver
The numbers of samples with associated gold and silver analyses are much smaller than for copper or molybdenum and represent only 38% of the database of samples >0.10% Cu. The Morenci deposit is a gold-poor porphyry system and overall contains less than 0.001 oz/ton Au (0.03 PPM) (the Morenci detection limit). Gold occurs in the Garfield fault, and is generally richer in the less altered margins of the deposit and in the peripheral veins to the northeast and southwest of the district (Lindgren, 1905a; Moolick and Durek, 1966). The Morenci deposit, however, is relatively silver-rich, and contains an average of 0.05 oz/ton (1.7 PPM) Ag with a silver to gold ratio of ~60 to 1 in this small data set. In general, silver appears to be associated with gold, however, silver also occurs as late stage silver-manganese oxide fissure veins throughout the district (Preece, Stegen and Weiskopf, 1993). The fissure veins predominantly occur in Paleozoic sedimentary rocks, and can be found over 10 km (6 mi) from the center of the district. Moolick and Durek (1966) reported that gold and silver were enriched up to two or three times in the upper part of the enriched blanket or near the base of the oxidized zone, however, this does not appear in the database statistics (Table 14). Unfortunately, there were not enough data points to make meaningful contour maps for gold and silver or establish any recognizable pattern.

**Distribution of Supergene Mineralization**

The distribution of supergene mineralization varies as a function of the regional and local geologic conditions. These conditions include protore and host rock composition, tectonic and geomorphologic history, climate and weather, faults and fracturing in the
vadose zone, position and migration of the water table, and chemical and mechanical erosion rates. Thus, a combination of factors competes to create, destroy or preserve supergene mineralization. Variations in the distribution and character of supergene mineralization are shown in the geologic maps and cross-sections referenced above and discussed below.

Pyrite-to-Chalcocite ratios

Pyrite-to-chalcocite ratios in the enriched blanket are related to both hypogene and supergene processes. The average total sulfide content in the enriched blanket is between 3.5 to 4 wt.% (Table 16) or slightly higher than in the underlying hypogene zone. Chalcocite averages 0.65 wt.% and ranges from 0.09 to over 3.5 wt.%. The highest chalcocite contents occur in Metcalf and Morenci and correlates with the highest-grade portions of the enriched blanket. Pyrite averages 3.1 wt.% and ranges from 0.02 to over 17 wt.%. Overall, the highest pyrite contents correspond with the higher-grade chalcocite zones in the Metcalf and Morenci areas. In general, there is an excellent spatial correlation between py/cpy ratio in the hypogene zone (Figure 37a) and the py/cc ratio in the overlying enriched blanket (Figure 37b), and probably reflects primary pyrite zoning in the district.

Although data are somewhat sparse for the central portions of the Western Copper and Morenci pit areas, and for the northwestern area of the district, several relationships are apparent. Overall, pyrite-to-chalcocite ratios average 6.5 to 1, and range from 0.2 to over 34. Zones with ratios >8 to 1 occur in parts of the district with high py/cpy ratios in the hypogene zone and represent areas where there was very little copper relative to pyrite.
initially. The <4 to 1 py/cc isopleths occur in the central portion of the district and are coincident with areas of low py/cpy ratios in the underlying hypogene zone (Figure 37). Overall, there are strong northwest-trending and northeast-trending alignments of low py/cc contours that are coincident with the structural fabric in the district (Figures 10 and 37).

Grade x Thickness

Grade x thickness maps for each supergene population provide the most insight about the distribution of mineralization across the district (Figure 38). The map shows isopleths of copper grade multiplied by the thickness of the drill hole interval in each zone. Equation (6) shows that the grade x thickness product is actually a proxy for the mass of copper represented by a particular drill hole interval. Integration of the area between isopleths would yield an estimate of the total contained copper content.

\[(6) \text{Cu-tons} = [(L_{\text{comp}})*(\text{wt.}\% \text{Cu}_{\text{comp}})] \times [(\text{frac}_{\text{Cu}}/100\%)] \times [(\text{Area}-L^2)\times(\text{tons}_{\text{rock}})/L^3] \]

where:

\[L_{\text{comp}} = \text{total length of the composite in the population from a drill hole}\]
\[\text{wt.}\% \text{ Cu}_{\text{comp}} = \text{average copper content for the composite}\]
\[\text{frac}_{\text{Cu}}/100\% = \text{conversion of wt. }\% \text{ to fraction of copper}\]
\[\text{Area}-L^2 = \text{area of influence for a particular composite}\]
\[\text{tons}_{\text{rock}}/L^3 = \text{tonnage factor from bulk density and specific gravity measurements.}\]
The composite supergene profile covers over 19 km$^2$ (7.5 mi$^2$) and averages almost 239 m (783 ft) thick across a range from 10 m (30 ft) to over 600 m (1,970 ft). On average, each successively deeper zone is thicker than the zone above. For the purposes of this analysis, the base of the supergene zone is defined as the contact between the enriched blanket (population 3) and the underlying hypogene zone (population 4), although weak supergene effects are still evident below this contact. Minimum and maximum thicknesses for each zone are very similar, which is a reflection of significant local differences in the enrichment profiles. Overall, the composite profile has an average grade of 0.32% Cu and contains an average of 77 m-% (251 ft.-%) of copper. The 90 m-% (300 ft.-%) contours for the composite supergene profile (Figure 38d) outline significant copper resources in the Morenci, Western Copper, Metcalf, Northwest Extension, Coronado, and Garfield areas. With the exception of Coronado, the bulk of the supergene mineralization occurs in the central graben (Figure 10). The best supergene mineralization at Coronado occurs in a smaller graben in between the Coronado and Keystone faults, and along the contact with the older granite porphyry stock (North and Stegen, 1993, Young-Mitchell et al., 1999). Differences in the character of mineralization and the enrichment profile in each area are a function of the local geologic conditions.

**Leached capping:** The distribution of copper in the leached capping is shown in Figure 38a. Because this zone is significantly depleted in copper, the grade x thickness contours reflect thickness differences more than grade variations across the district. Values average only 6 m-% (19 ft.-%) and range from <1 to 50 m-% (163 ft.-%) (Table 16). Significant thicknesses of leached capping occur predominately in a roughly east-
west-trending oblate zone in the Northwest Extension and Metcalf areas in the central portion of the district where it can be up to 463 m (1,520 ft) thick (Figure 31). Relatively thick leached capping also occurs on the eastern side of Chase Creek in the Garfield area. Significant thicknesses of leached capping were absent above the enriched blanket in the Morenci pit, and are absent in the exterior portions of the Coronado, Garfield, Metcalf, and Western Copper areas (Figure 38). Leached capping occurs in all rock types, alteration zones, and with variable pre-cursor sulfide contents, but in highly variable thicknesses. Presumably, the distribution of leached capping reflects the extent of weathering and erosion across the district. Erosion has outpaced leaching in the peripheral areas where near-surface sulfide mineralization occurs beneath the ridge crests and in some of the surrounding drainages that have incised through the profile (Figure 39d). The remaining thick leached capping may be related to preservation beneath topographic highs in the center of the district as well as to geologically younger deep leaching along structures such as the War Eagle fault in the Metcalf area (Figure 31).

**Partially leached:** The distribution of copper in the partially leached zone is somewhat coincident with the leached capping as shown in Figure 38b. The partially leached zone contains pre-existing enriched zones that have been oxidized *in-situ* or partially leached and retain a significant, but partially depleted copper content. This is reflected in the grade x thickness contours which tightly outline the oxide copper bodies in the Northwest Extension and Garfield areas, and broadly define the partially leached sulfide zones at Metcalf. These zones are also well displayed in cross section in Figures 31 and 32. Values still only average 25 m-% (82 ft.-%) but range from <1 to almost 180
m-% (600 ft.-%) (Table 16). These areas closely correspond to areas in the underlying enriched blanket with py/cc ratios <4 to 1 (Figure 37b). In these areas, it is likely that there was not enough pyrite left in the pre-existing enriched zone to oxidize and completely leach the remaining chalcocite.

**Enriched blanket:** The distribution of copper in the enriched blanket is widespread across the district as shown in Figure 38c. In this zone, the grade x thickness product is a function of significant variations in both copper grade and zone thickness. Values are significantly greater than in the overlying zones and average 65 m-% (212 ft.-%) with an extreme range from 1 to over 397 m-% (2 to over 1,300 ft.-%) (Table 12). The 76 m-% (250 ft.-%) contour outlines the original Clay orebody of Moolick and Durek (1966) in the Morenci area, and the higher-grade and thick enriched zones in the Metcalf, Western Copper, and Coronado areas. The bulk of the copper in the enriched blanket (Figure 38c) is coincident with those areas having the highest-grade hypogene mineralization at depth (Figures 33), the highest total sulfide content, and py/cpy ratios between 2 and 8 to 1 (Figure 37b). These areas are further coincident with the monzonite porphyry (Figure 28) and its attendant pervasive quartz-sericite-pyrite (QSP3) alteration (Figure 29). The bulk of the enriched blanket at Western Copper has a covellite-chalcopyrite mineral assemblage, however, and is associated with a zone of low pyrite content and low py/cpy ratios in an area of overlapping quartz-sericite-pyrite (QSP2) and potassic (K2) alteration. Throughout the rest of the district, the enriched blanket averages between 15 and 76 m-% (50 and 250 ft.-%) beneath variable thicknesses of leached capping.
Pre-mine topography: In general, the supergene profile closely follows pre-mine topography. Figures 30, 31, and 32 provide a cross sectional view of the variations in thickness of the enriched blanket and overlying leached zones and their relationship to pre-mine topography. In places, Chase Creek and several of its tributaries have deeply incised the enriched blanket. This is apparent in the King and Placer drainages in between Garfield and Metcalf, in the Santa Rosa Canyon drainage north of Coronado, and in the lower Chase Creek area between Morenci and Western Copper (Figures 38 and 39d). The enriched blanket thins to less than 15 m (50 ft) beneath the higher ridges that form the drainage divide between the Morenci hydrologic sump (Dames and Moore, 1995) and the Eagle Creek and San Francisco River drainages (Figures 38 and 4). This is the same general area where the hypogene copper grade diminishes to 0.05% Cu, py/cpy ratios increase to >8 to 1, and the drill hole pattern ends.

Water table: Figures 30, 31, and 32 show the location of the water table relative to the enriched blanket across the district. Mining has locally affected the water table elevation, particularly in the Morenci and Metcalf pits. Elsewhere in the district where mining has not progressed very deeply, the water table should be fairly close to its location during Holocene to Recent time. In many areas of the deposit, the enriched blanket is elevated up to 250 m (820 ft) above the water table, an observation that Lindgren (1905a) made prior to open pit mining.
Enrichment Factors

Enrichment factors provide an indication of the relative upgrading in copper content and are shown in a map of lateral gains and losses in the supergene profile (Figure 39a). Overall, the average enrichment factor is 2.9 and fairly uniformly distributed across the district. With few exceptions the >1 contour encompasses the entire enriched blanket. Although enrichment factors are relatively uniform, they locally range from 0.3 to 35 (Table 16). The highest values occur in Paleozoic sedimentary rocks in the Garfield, Shannon, and Southside areas, and in the thickest and highest grade portions of the Morenci, Metcalf, and Coronado enriched zones. Relatively high values (>5) also occur in the central younger granite porphyry intrusive complex and in Proterozoic granite in peripheral areas of the district associated with low hypogene grades at depth. The >3 contour occurs almost exclusively within the central graben (Figure 39a and 10), but is not always associated with richer parts of the enriched blanket. Areas with enrichment factors <1 occur in along the margins of the district and are surrounded by volumes with only slightly better enrichment.

This overall pattern suggests that copper may have been transported from the topographically higher and peripheral areas of the deposit and deposited in the enriched blanket in the central graben because of district flow in this structural setting (Figure 4). This area is coincident with the higher-grade hypogene mineralization and most intense hydrothermal alteration (QSP<sub>3</sub>). In this setting, laterally migrating solutions would have added copper to an already well-mineralized structural domain.
Calculated Eroded Thicknesses

The calculated values for eroded thickness have been contoured and displayed as an isopach map in Figure 39b. Because the calculations were done for vertical columns and then displayed as point values, neither lateral copper fluxes nor slope diffusion components were integrated into the equation. Therefore, the results are probably more meaningful as area-integrated average eroded thicknesses than as local point values. Overall, eroded thickness is relatively uniform across the district and averages only 0.3 km with local variations that range from −0.3 km (−975 ft) to almost 2.8 km (9,078 ft) (Table 16). Clustered data points >0.3-km (>1,000-ft) thick in parts of the Morenci, Metcalf, Northwest Extension, and Garfield areas are spatially associated with the older granite porphyry intrusive complex. The large cluster of thicker points in the Morenci pit area is coincident with the monzonite porphyry and the thick, high-grade enrichment blanket in the original Clay deposit. Overall, the thicker areas are generally confined to the central graben.

These patterns lead to the conclusion that the generally thin to negative eroded thicknesses to the west of the Morenci and Northwest Extension areas indicate areas with relatively depleted copper contents and may be the source regions for copper in the Chase Creek graben. This is consistent with Cook’s (1994) conclusion that there was “profound lateral migration” of copper at Morenci.

Pre-enrichment Paleotopography
A contour map of the theoretical pre-enrichment paleotopographic surface is shown in Figure 39c. In general, the reconstructed paleotopography has a mean elevation of about 1,882 m (6,173 ft) and ranges from 1,241 to 4,350 m (4,070 to 14,269 ft) above modern mean sea level (Table 16). This is not that much higher than the pre-mine average topographic surface elevation of about 1,700 m (5,580 ft). Although locally there are numerous unnatural spikes in the topography from the point data, as described in the section above, the smoothed overall topography appears reasonable (Figure 39c). Clusters of data points with elevations higher than about 2,100 m (7,000 ft) occur within the Chase Creek graben. These areas are also coincident with the thicker and higher-grade portions of the enriched blankets at Morenci and Metcalf and with the oxide copper body at Northwest Extension. These same areas are coincident with the monzonite and older granite porphyry intrusive complexes in the center of the district.

In general, the paleotopographic lows are coincident with the modern, pre-mine drainage patterns (Figure 39d). This would not be unexpected because the reconstructed paleotopographic surface was derived from the pre-mine topography and the calculated eroded thicknesses. The interesting aspect of this pattern, however, is that the modern, pre-mine drainage patterns show a relatively close correlation with the paleotopographic surface. Drainages in Garfield Gulch, King and Placer Canyons, Coronado and Santa Rosa Gulches, and all along lower Chase Creek conform to the paleotopography. Only in a few areas at Metcalf and Morenci are there modern drainages that cross paleotopographic highs.
These relationships lead to the conclusion that supergene enrichment at Morenci is a geologically young feature and is related to the processes of chemical weathering and erosion that created the modern physiography of the district. This conclusion is further supported by the morphology of the supergene zone and the generally close relationship of the enriched blanket to pre-mine topography.

**Character of Supergene Mineralization**

The character of supergene mineralization varies systematically across the district as a function of local geologic conditions. A generalized enrichment profile for the Morenci district is shown in Figure 40. Although this general profile occurs throughout the district, the character of mineralization and the relative thickness of the zones vary significantly from place to place. These variations are shown in the three principal cross sections through the district (Figures 30, 31, and 32) as well as in cross sections for the Metcalf (Figure 41), Northwest Extension (Figure 42), and Morenci (Figure 43) pit areas. The suite of mineralization cross sections on 610-m (2,000-ft) centers were developed from the research database in combination with detailed mineralogical profiles for selected core holes along the line of the three principal sections. Two examples of mineralogical profiles in core hole #1126 from Northwest Extension, and #1193 from Morenci are shown in Figures 44 and 45, respectively. An interpretation of the multiple, stacked supergene zones in a portion of the Chase Creek graben is shown in Figure 46. Copies of all the sections are available in the Phelps Dodge Morenci, Inc. Geology office.
In addition to the descriptions on the geologic logs for these core holes, character samples were selected for X-ray diffraction analysis, reflected light study of polished sections, and electron microprobe study. Photomicrographs of representative mineralization from the polished section suite are shown in Figures 47 and 48.

Descriptions of the polished sections from Castro-Reino (pers. commun.) are included in Appendix D. Supplementary detailed thin section descriptions are available in Calkins (1997). Table 11 contains a list of the common supergene minerals at Morenci and their chemical formulas.

The characteristics of supergene mineralization are described below in the context of the areas in which they are best displayed. Although each mineralized area contains unique features, they generally represent variations of the styles described below. Detailed study of each of these areas was out of the scope of this study. The Morenci staff remains the experts on these areas.

Leached Capping

**Metcalf example:** Leached capping occurs in variable thicknesses across the district, but is probably best displayed in the Metcalf area (Figures 38a and 41). In general, mineralization in Metcalf occurs almost entirely within the monzonite and the older and younger granite porphyry intrusive complex (Figure 28). In this area, the War Eagle fault exerts a strong control on the supergene profile, both offsetting enrichment and controlling deep leaching and enrichment in the hanging wall of the fault zone (Figure 41). Pervasive QSP$_3$ and moderate QSP$_2$ hypogene (Calkins, 1997) quartz-sericite-pyrite
alteration overwhelm the original texture of the monzonite and older granite porphyry host rocks. The rocks have been intensely fractured and veined, with fracture densities ranging from about 0.25 to over 0.40/cm in places.

Metcalf contains a classic, but tilted, enrichment profile (Figure 41) that consists of a 200-m thick zone of leached capping (0.06% Cu) that overlies a 180-m (590-ft) thick enriched blanket (0.42% Cu). In the southern part of the Metcalf pit, leached capping is over 450 m (1,475 ft) thick. Copper grades in the leached capping display a gradual increase with depth from 0.02 to about 0.11% Cu. The leached capping has an abrupt contact with the composite enriched blanket below. In places, however, the upper 90 meters (295 ft) of the enriched blanket has been partially leached. Partial leaching is also well displayed as relatively narrow, oxidized fractures that penetrate approximately 180 to 270 meters (590 to 885 ft) into the enriched blanket exposed on the east-side of the Metcalf Pit wall.

**Mineralization:** Leached capping consists of a stockwork of quartz + hematite +/- goethite +/- jarosite veins and veinlets left behind as a result of nearly complete leaching of the precursor pyrite and chalcocite mineralization. In places, hematite boxworks are common and appear as 0.1 to 1 mm features that form a sponge-like or honeycomb surface on open fractures. These boxworks are soft and leave a maroon-red streak characteristic of hematite that has replaced chalcocite (Blanchard, 1968). These boxworks have been interpreted to represent the destruction of a pre-existing chalcocite enriched blanket at Metcalf during Miocene to Pliocene time (Tittley and Marozas, 1995; Tittley and Enders, 1998; Moolick and Durek, 1966; Langton, 1973; North and Preece, 1993; Cook, 1994;
Enders et al., 1998b). In other areas, a mixture of brown, powdery goethite + hematite +/- jarosite are common, and are often associated with silica boxworks after pyrite. Oxidized quartz + pyrite +/- sericite veins contain a fine mixture of 0.5 to 2 mm thick, yellow powdery jarosite and silica in a quartz boxwork. Elsewhere, variable mixtures of transported hematite +/- goethite +/- jarosite occur as paint or thin coatings on fracture surfaces.

Copper in the leached capping occurs as remnant sulfide, oxide, carbonate or sulfate minerals. Where leached capping grades into zones of partial leaching, the rocks may contain pervasive oxidation along veins with hematite in the sericite selvages that are in sharp contact with un-oxidized pyrite and chalcocite in the interior of the rock. In other areas, copper occurs in small amounts as neotocite, tenorite, cuprite, native copper, malachite, brochantite, or chrysocolla (Table 11). Copper oxides may also be tied up as micron-size particles of copper carbonate and silicate minerals inter-grown with iron hydroxides, mineraloids, and gangue in the leached capping. The possibility of copper occurring in lattice substitution within the hydrous or non-hydrous iron oxides as well as in the complex cupiferous Fe-Mn-(Ca-Si)-bearing oxides/hydroxides cannot be ruled out, as some of the ill-defined Cu-Mn-phases or mineraloids are known to contain this type of copper occurrence in northern Chilean oxide copper deposits and SW Arizona (Baum., pers. commun.).

Alteration: Leached capping retains the strong supergene argillic alteration commonly found with the underlying enriched blanket, described below. Kaolinite commonly occurs along fractures and veins in the leached capping as a result of intense
local acid attack of the wall rock from dissolution of pyrite. Iron oxides also occur
pervasively throughout the groundmass of the rocks imparting a reddish color to the
kaolinite and staining all of the rocks in this zone. The dominant clays are smectites.

Alunite veins are common in the district, and some show evidence of multiple
generations of alunite deposition. Alunite +/- jarosite +/- kaolinite occurs in 0.1 to 1-cm
wide veins and as fracture filling in the leached capping. Individual veins typically cross
cut the quartz-sericite +/- sulfide or iron oxide stockwork and have very sharp contacts
with weakly to strongly sericitized wall rock. Alunite also commonly fills pre-existing
quartz + sericite + hematite veins and contains “clasts” of remnant wall rock and oxidized
sulfides. In some samples, alunite appears to have filled open-spaces after hematite
cemented the fractured wall rock. Alunite is microcrystalline and typically white to
yellow and pistachio green in color. It generally occurs intermixed with silica and
kaolinite in variable amounts and with small amounts of sericite from the wall rock,
although very pure alunite veins occur in places. In some places, alunite appears to be
admixed with small amounts of jarosite. Veins of jarosite and jarosite+alunite occur in
some of the higher elevations in the Metcalf pit. Selected samples of alunite are described
in more detail in Appendix E and in the Geochronology chapter below.

Partially Leached

As defined in the population descriptions in the Database Evaluation and Modeling
section, partial leaching represents in-situ oxidation (without significant transportation) or
partial leaching of sulfide minerals of the present, or an earlier-cycle, enrichment blanket.
Partial leaching of sulfide minerals is a manifestation of the same weathering processes that formed the leached capping and is described in the section above. *In-situ* oxidation at Morenci is described below.

**Northwest Extension example:** *In-situ* oxidation of pre-existing supergene sulfides occurs in the Metcalf and Garfield areas (Figures 32 and 38b), but is probably best displayed at Northwest Extension (Figure 42). In general, mineralization at Northwest Extension occurs in Proterozoic granite and in the older and younger granite porphyry intrusive complex (Figure 42). Moderate QSP$_2$ and weak QSP$_1$ hypogene (Calkins, 1997) quartz-sericite-pyrite alteration affects the older granite porphyry and the younger granite porphyry and Proterozoic granite, respectively. Primary hypogene and secondary supergene mineralization occur as a stockwork of veins and veinlets with a fracture density ranging from about 0.10 to 1.0 per cm and averaging 0.13 per cm (Preece, 1989). The dominant structural feature of Northwest Extension is the northerly striking, 60-80° easterly dipping, 15- to 30-m (50- to 100-ft) wide Las Terrazas fault zone and its associated splays and subsidiary structures, most notably the north-northwest-striking Drumlin splay in the northern footwall.

The Northwest Extension deposit contains a 250-m (820-ft) thick body of enriched (0.43% Cu) copper oxide mineralization bounded by low-grade (0.05% Cu) leached capping above and below. The copper oxide mineralization and leached capping overlie a relatively thin 15- to 45-m (50- to 150-ft) thick, high-grade (0.64% Cu) sulfide, un-oxidized enriched blanket (Figure 42). The copper oxide mineralization is generally constrained to the hanging wall of the Las Terrazas and Drumlin faults on the west and is
bounded by the younger granite porphyry stock on the east. Copper oxide mineralization in the partially leached zone, and the underlying sulfide blanket are contiguous with the Morenci deposit to the south but gradually diminish in grade towards the north. For a more detailed description of the Northwest Extension deposit see Preece (1989), and Melchiorre and Enders (in prep).

**Mineralization:** Copper oxide mineralization is zoned with depth at Northwest Extension as represented in the profile from drill hole #1126 (Figure 44). In general, copper oxide minerals at Northwest Extension consists of various amounts of: chrysocolla, brochantite, and malachite, plus the black copper oxide minerals tenorite, neotocite, and various other copper-bearing manganese oxides (Table 11). These occur along with copper-bearing clays (kaolinite) and the limonite suite of iron oxide minerals hematite, goethite, and jarosite. Hematite +/- goethite and jarosite persist to depths of over 340 m below the surface. Minor amounts of cuprite and rare native copper occur in localized zones in the leached capping or at the top of the sulfide zone. Azurite appears to be restricted to local accumulations in the Las Terrazas fault. Brochantite + black copper- manganese oxides appear to dominate below the zone of malachite+/-azurite mineralization.

A strong zone of manganese-oxide mineralization occurs at the base of the oxide zone in the Las Terrazas fault. X-ray diffraction analyses (Vieira, pers. commun.) of this mineralization revealed that it contains a mixture of cryptomelane, hollandite, hausmannite, and todorokite in addition to a zinc-manganese-oxide mineral (Zn$_2$Mn$_3$O$_8$) (Table 11). These minerals occur with variable amounts of quartz and sericite. Cryptomelane and
hollandite contain potassium and are dateable using the $^{40}\text{Ar}/^{39}\text{Ar}$ method (Vasconcelos et al., 1994b). These samples are described in more detail in Appendix E and in the Geochronology chapter below.

One sample of banded oxide mineralization was collected from the Azurite pit, in the Southside area of Morenci, for detailed study at New Mexico Tech in Socorro. Because the blue-green mineraloids were amorphous, electron microprobe analysis was required. Chavez (pers. commun.) reported results from one patch of mineralization:

“Microprobe data suggest that the blue-green minerals are “chrysocolla” but have variable copper contents ranging from about the high 20’s to low 40’s in wt-% Cu. Manganese is scant, as is iron; some samples may have 0.X wt-% of these components, although I suspect that at least some Fe-oxides may be contaminating the Fe values. Silica, as SiO$_2$, contents are variable also, but average about 25-45 wt-%. Interestingly, because of the water contents of these blue-green minerals, the samples decrepitate substantially during probe beam heating, but analyses with wide (20-40 micron) beams mimic those of narrow (10 micron) beam analysis. Cloudy-white “chrysocolla” is impoverished in copper and probably shows silica enhancement via mass loss; blue chrysocolla has the greatest copper contents, and green chrysocolla has traces Fe and/or Mn, in general.”

Mineral bands in the oxide zone are interpreted to represent cyclical deposition of oxide minerals as a result of transportation and deposition of minerals, and reduced carbon from bacterial blooms during flushing events associated with storms, seasons, or climate changes coupled with tectonic events (Melchiorre and Enders, in prep.). Deposition as a particular mineral is a function of the local geochemical environment as well as solution chemistry at a particular time.

A variety of other copper oxide minerals have been identified in the district (Lindgren, 1905a; Moolick and Durek, 1966). Most notably, this includes dioptase at Northwest Extension and libethenite at Coronado and Northwest Extension, and olivenite
and conicalcalcite at Garfield and in the outlying prospects around the district. Rare metatorbernite has also been reported at Coronado (North, pers. commun.). Lindgren (1905a) reported spangolite and gerhardtite at Metcalf. A detailed mineralogical study of the district would likely reveal a variety of other, less rare minerals.

**Alteration:** Supergene argillic alteration in the partially leached zone retains the characteristics of both the leached capping and enriched zone described in the section above and below. Kaolinite +/- alunite +/- quartz locally occurs as veins and fracture filling in the partially leached zone and contains traces of remnant partially oxidized pyrite, chalcocite, and chalcopyrite.

**Enriched Blanket**

A supergene sulfide enrichment blanket occurs in some form virtually everywhere in the Morenci district (Figure 38c). In detail, the enrichment blanket is a composite of zones of distinctive secondary copper minerals with gradational boundaries that overlap in space and time in response to the structural evolution and changing chemical environment of the district. Following the nomenclature of Lichtner and Biino (1992), the enriched blanket can be subdivided into three zones: 1) the enrichment zone at the top of the blanket, 2) the middle blanket in which chemical reactions conserve copper in the solid phase and no further enrichment occurs, and 3) the nascent blanket that continuously forms at the interface with the hypogene protore at depth under dynamic chemical and hydrological conditions (Figure 40). This is a generalized vertical sequence, and not every zone is present or well developed throughout the enriched blanket.
In the Morenci district, a single-stage profile typically contains a chalcocite +
djurleite >> covellite or chalcopyrite assemblage in the enrichment zone, a covellite +/-
chalcocite and chalcopyrite assemblage in the middle blanket, and a chalcopyrite >>
chalcocite or covellite assemblage in the nascent blanket such as at Metcalf (Figure 41).
Covellite appears to be ubiquitous throughout the enriched blanket, but higher-grade
covellite typically occurs in distinct zones or layers in the enriched blanket that range from
a few meters to over 100 m (300 ft) in thickness. Covellite occurs widely, but not
uniformly at the top of the enriched blanket in the Morenci and Metcalf areas (Moolick and
Durek, 1966, Preece, 1981). The contact with leached capping above the enrichment zone
is generally very sharp. Lindgren (1905a, p. 203-204) also noted that the contact with the
“pyritic zone” (middle blanket) below was also sharp and marked by grade changes over 3
to 6 m (10 to 20-ft) from >2 to 5% to lower grades below in the Joy, Montezuma, and
Reyerson mines. In many places in the Morenci district, the nascent zone at the bottom of
the enrichment blanket grades imperceptibly into protore below over hundreds of meters
(Figures 43 and 44). In these zones, analytical techniques such as the ferric-soluble copper
method (MLT) are required to determine the contribution of copper from chalcocite to the
total copper content in the zone.

In general, the Morenci district contains single-stage profiles along the western and
eastern margins of the deposit and in several other structural domains. In the central Chase
Creek graben, however, the supergene zone contains evidence of multiple-stage enrichment
profiles. Evaluation of 44 core holes along and in between the three principal cross
sections showed that 20 of these holes contained some evidence of multiple-stage enrichment (Figure 10).

Morenci example: Nowhere in the district is the enrichment blanket as well developed as in the historic Morenci pit area (Figures 42c and 47). Mining in this area was completed in early 1996 and most of the pit has now been back-filled with leach stockpiles. Most of the information about this area is from historical accounts or preserved in core. Much of the deposit was poorly drilled in the early open-pit days and the drill hole record for the central part of this area is incomplete (Figure 35). Fortunately, several deep drill holes were completed and well studied that provide a good record of the mineralogical profile.

Mineralization in the Morenci pit area occurs in the monzonite and quartz monzonite porphyry stock and in Proterozoic granite and granodiorite, and the overlying Paleozoic section where these rocks have been intruded by a monzonite porphyry and older granite porphyry dike swarm (Figures 28 and 30). Laramide-age diabase intrudes parts of the Quartzite fault and also contains mineralization (Plate 1). Intense (QSP$_3$) and moderate (QSP$_2$) hypogene quartz-sericite-pyrite alteration (Calkins, 1997) overprints earlier potassic and quartz-magnetite alteration (Wright, 1997). Primary hypogene and secondary supergene mineralization occur in a well-developed stockwork of veins and veinlets with an average fracture density of 0.9/cm and a range from 0.2 to 2/cm (Preece, 1981). The thickest and highest-grade supergene mineralization is roughly coincident with higher-grade hypogene mineralization (Figures 33 and 38c) and occurs in the Chase Creek graben between the southwesterly dipping Kingbolt fault and the northeasterly dipping Copper
Mountain fault. The Quartzite fault typically bounds this mineralization to the south (Figures 10 and 38c). The Niagara fault offsets the enriched blanket in the Chase Creek graben, and strikes southeasterly through the middle of the Morenci pit and splays into numerous branches as the fault approaches the Quartzite fault (Wright, 1997).

The Clay deposit in the Morenci pit area contains a 360-m thick high-grade enriched blanket (0.90% Cu) beneath a relatively thin 10- to 95-m (30- to 310-ft) thick average grade (0.09% Cu) leached capping (Figure 45). At higher elevations, particularly west of the Apache fault but also in some of the upper portions of the main zone, the enriched blanket has been partially leached. The Copper Mountain fault bounds the thickest portion of the enriched blanket on the west and offsets the base of the blanket by about 85 m (280 ft). The fault contains zones of brecciated porphyry and sedimentary rocks, and includes fragments of chalcocite that indicate the enriched blanket had at least partially formed prior to this period of movement (Lindgren, 1905; Walker, 1995). The Kingbolt fault bounds the eastern side of the blanket and juxtaposes enrichment against low-grade, pyrite-chalcopyrite hypogene mineralization of the Western Copper deposit in the footwall. The fault contains chalcocite veins that occur as stringers in the fault that wrap around clasts and fill void spaces in the matrix, which are further brecciated in places attesting to multiple episodes of movement on this fault (North and Stegen, 1993).

Mineralization: Supergene copper sulfide mineralization in the Morenci pit occurs in as many as three distinct, stacked profiles (Figure 46). This results in fairly complicated overlapping mineral assemblages in the enrichment profiles. Evidence for this occurs in drill holes MO-1, MO-2, #1-991, #985, and #1193. This zoning is well represented in the
profile from drill hole #1193 (Figure 45). This profile displays a complete sequence from the enrichment zone between 0 and 127 m (415 ft), to the middle blanket between 127 and about 175 m (415 and 575 ft), and the nascent blanket between 175 and 300 m (575 and 985 ft) in depth. A second, lower enrichment zone occurs from 300 m (985 ft) to the bottom of the hole at 456 m (1,495 ft).

The enrichment zone contains 0.1 wt.% to over 2 wt.% chalcocite as replacements, or fracture fillings and coatings, and rims of pyrite and chalcopyrite. The drill hole log for hole #1193 noted digenite in this upper portion of this zone, but reflected light study of a polished section from 23 m (75 ft) revealed the mineral to be locally inter-grown covellite. The lower portion of the enrichment zone contains chalcocite with trace amounts of covellite in places. A sample from 50 m (164 ft) contained four mineral domains that showed classic replacement textures (Figure 47a). In this zone, enrichment is nearly complete with conversion of chalcopyrite to medium dark grey chalcocite, and partial conversion of pyrite to medium dark grey chalcocite along fractures and grain boundaries. Deeper in the enrichment zone, replacement is less complete. A sample from 72 m (235 ft) shows a wide variety of chalcocite replacement textures (Figure 47b). Fine-bladed covellite and later bluish grey chalcocite subsequently replaced early, coarse-bladed covellite that penetrated crystallographic planes in chalcopyrite. A sample from 78.5 m (257.5 ft) (Figure 47c) contained, medium to dark grey chalcocite replacing fine-grained, extremely comminuted pyrite, and comminuted chalcocite and covellite in local fracture zones. Chalcocite replacement appears more intense and complete in the more heavily fractured areas. Supergene sulfide comminution is also evident in a sample from 79 m
(259 ft) where medium dark grey and dark bluish grey phases of chalcocite replace chalcopyrite and bornite. This fragmental, cataclastic texture is also evident in a sample from 80 m (262 ft) that exhibits local fracturing and chalcocite cementing pyrite.

The middle blanket contains a mixture of 0.05 to 1.4 wt.% chalcopyrite, with 0.1 to 0.4 wt.% covellite and trace amounts of chalcocite replacing chalcopyrite and pyrite. Covellite occurs as blades penetrating chalcopyrite cleavage planes, which have been replaced by medium grey whitish chalcocite, like that shown in Figure 47b.

Chalcopyrite + covellite mineralization in the middle blanket grades imperceptibly into the low-grade chalcopyrite-dominant assemblage in the nascent blanket below. In this zone, chalcopyrite contents range from only 0.01 to 0.4 wt.% with a trace to 0.2 wt.% covellite, and rare chalcocite. The lower, weakly enriched zone in drill hole #1193 contains elevated copper contents and a mixture of chalcocite, chalcopyrite, bornite, idaite and magnetite. A sample from 172 m (565 ft) (Figure 47d) shows chalcopyrite replaced by bornite + idaite, subsequently replaced by medium grey whitish chalcocite. Although chalcocite only averages 0.05 wt.% across this zone, it accounts for 35% of the total copper content in the lower enriched zone.

XRD and microprobe studies on “chalcocites” from the Morenci district reveal that copper to sulfur ratios vary from 2.0 to 1.6 (Mazdab, pers. commun.). Black “sooty” chalcocite (Cu$_2$S) occurs throughout the district and is typical of many other enriched porphyry copper deposits. “Steel glance” chalcocite is a common copper mineral in porphyry copper deposits (Roseboom, 1962), and occurs near the upper portions of the enrichment zone throughout the Morenci district and yields typical djurleite (Cu$_{1.96}$S) XRD
patterns. Djurleite at Morenci typically occurs in massive veins up to 1 cm wide and as smaller masses almost completely replacing pre-existing pyrite. Digenite (Cu$_{1.8}$S) has been reported from the Morenci district (Preece and Menzer, 1992), but polished section studies indicate that this may be widely mistaken at Morenci for covellite. Digenite is actually a member of the Cu-Fe-S family and can contain small amounts (~1%) of iron (Craig, 1974; Morimoto and Koto, 1970). At temperatures <70°C digenite is metastable and decomposes to mixtures of anilite (Cu$_{1.75}$S) and djurleite (Morimoto and Koto, 1970; Morimoto and Gyobu, 1971). Both anilite and mixtures of anilite and djurleite have been identified in Morenci samples using microprobe analysis and reflected light microscopy. One sample of geerite (Cu$_{1.59}$S) from Metcalf was identified using microprobe analysis. Geerite is one of the intermediate secondary sulfides in the chalcocite-covellite replacement series (Sikka et al., 1991). Electron microprobe studies of samples of djurleite, anilite and geerite from the Morenci district indicate they contain an average of 314-PPM silver (Mazdab, pers. commun.).

**Alteration:** Supergene argillic alteration in the Morenci district occurs in veins and as pervasive, white to beige and yellow clays that alter feldspars and remnant biotite in the host rocks. Using petrographic, XRD, and stable isotope studies, Calkins (1997) identified the supergene phyllosilicate as kaolinite that ranges from selective replacement of plagioclase phenocrysts, to pervasive replacement of all groundmass and feldspar phenocrysts. In some areas, argillic alteration is so intense that sericite in feldspars and in the groundmass has been converted to kaolinite (Calkins, 1997). In other zones, weaker argillic alteration appears as kaolinite replacing sericite in plagioclase, and sericite
replacing biotite phenocrysts (Calkins, 1997). In general, the degree of supergene argillic alteration is inversely proportional to the intensity of hypogene quartz-sericite-pyrite alteration. Nonetheless, supergene argillic alteration of felsic igneous rocks corresponds with pyrite abundance, and the monzonite porphyry appears to be the most intensely supergene argillized rock in the district, followed by the older granite porphyries, with weaker development in the Proterozoic granite. This may be due, in part, to the absence of primary framework quartz that can armor feldspars in other igneous rocks. Supergene argillic alteration is typically best developed in the upper few hundred meters of the deposit where it destroys the original rock texture in places. The intensity gradually decreases towards the bottom of the enriched blanket, but kaolinite +/- quartz veins persist even into the hypogene zone at depth. The iron-montmorillonite mineral nontronite occurs at the bottom of the oxide zone (Moolick and Durek, 1966; Calkins 1997).

Supergene argillic alteration also occurs on fractures inter-grown with supergene sulfides in pre-existing hypogene veins and in veins that cross cut all of the older stockwork mineralization throughout the district. Supergene-stage veins are a family of kaolinite +/- quartz +/- alunite +/- sericite veins that contain variable amounts of illite and jarosite that occur in the leached capping and persist to great depths in the enriched blanket and hypogene zone below. The supergene veins typically range from about 0.5 to 1 mm wide, and commonly occur as hairline fractures to veins up to 1.5 cm. They have very sharp contacts with the wall rock and contain remnant chalcocite, covellite, and pyrite that have been oxidized to hematite and jarosite in the leached capping. Veins with supergene minerals can be mono-mineralogical and contain only kaolinite, alunite, illite, or quartz.
More commonly, these veins contain a finely inter-grown mixture of quartz + kaolinite or quartz + alunite than makes hand specimen mineralogy extremely difficult. XRD analysis is typically required to distinguish mineralogy as discussed in more detail in the Geochronology chapter, below. Kaolinite + quartz veins are far more common throughout the district than alunite veins and persist to greater depths in the enrichment profile. Many of the “alunite” veins, reported in drill hole logs, are actually kaolinite + quartz veins upon closer inspection. Stable isotope studies (Calkins, 1997) indicate that the kaolinite veins are of supergene origin.

Sericite, montmorillonite, and kaolinite all occur in core from hole #1193. White chalky supergene clays consisting of a mixture of kaolinite and montmorillonite occur as pervasive replacement of the rock throughout the upper enrichment zone to a depth of 126 m. From 126 to 250 m (415 to 820 ft) clays are generally weakly developed or absent and correspond to the upper two thirds of the nascent blanket. From 250 m (820 ft) in depth to the bottom of hole yellow clays predominate. In this zone, the yellow clay replaces feldspars, particularly plagioclase and occurs on fractures throughout the zone. XRD study (Calkins, 1997) shows that some of this yellow clay is montmorillonite, as well as mixtures of kaolinite and illite (Titley, pers. commun). XRD analysis of a scraping of yellow clay from 374 m (1,227 ft) yielded a pattern consistent with the mineral diadochite [Fe₂(PO₄)(SO₄)(OH)₅H₂O] (Titley, pers. commun.). Moolick and Durek (1966) reported a chemical analysis of ½(Fe, Mg, Ca)O.Al₂O₃.5SiO₂.nH₂O for a “yellowish-brown montmorillonite (that) occurs below the chalcocite zone… and permeates most of the altered rock and that fills fractures for several hundred feet into the protore”.
Paragenesis

Although mineralization at Morenci is highly variable and contains multiple superfine mineral assemblages that overprint hypogene patterns, a general paragenetic sequence is evident as shown in Figure 49. This is based on reflected light microscopic studies of 24 polished thin sections (Castro-Reino, pers. commun.) from the supergene blanket at Morenci (drill hole #1193), Western Copper (drill holes #WC-50 and 60), and Garfield (drill hole #2135). In addition, observations from Northwest Extension (drill hole #1126, Figure 44) and other drill holes, along with hand sample examination provide further information about mineral paragenesis. Detailed polished section descriptions are included in Appendix D.

Primary Copper Mineralization

The general paragenetic order in the hypogene zone described below, although not strictly tied to hypogene vein assemblages, is nevertheless fairly straightforward. Early high-temperature intermediate solid solution (ISS – cp+po) mineralization is inferred to have occurred based on pyrrhotite lamellae in some chalcopyrite grains (Figure 48a). This was followed by initial chalcopyrite +/- pyrrhotite +/-bornite, and magnetite mineralization. The next period includes molybdenite and additional chalcopyrite +/- pyrrhotite +/- bornite mineralization. Chalcopyrite with exsolved sphalerite blebs is next followed by a late stage of chalcopyrite mineralization. Pyrite contains inclusions of chalcopyrite and occurs relatively late in the hypogene paragenesis. The last stage
typically displays pyrite replacing and rimming earlier chalcopryite, bornite and molybdenite.

Exceptions to this general sequence are not difficult to find. In Morenci, for example, chalcocite veins occur as massive, steely replacements of hypogene precursor sulfides and are, in turn, replaced by magnetite up to 300 m (1,000 ft) below the bottom of the blanket (Parker, pers. commun.). These and other conflicting relationships indicate additional work needs to be done on hypogene mineral paragenesis.

Secondary Copper Sulfide Mineralization

The paragenetic order in the enrichment phase of supergene mineralization is complicated by progressive mineralogical changes in space and time. At Morenci, there were multiple cycles of leaching and enrichment. In addition, the duration of enrichment and the geochemical gradients controlled the style and extent of replacement. Nonetheless, a general paragenetic order is evident, if not completely represented everywhere at Morenci, as shown in Figure 49. Chalcopryite appears to have been replaced before pyrite in all of the samples, but was not completely replaced in many of the grains (Figure 48b). Initial enrichment produced bornite +/- idaite as replacement of chalcopryite in some samples. In other places, covellite is preserved as the initial phase as coarse and fine blades that penetrate the {011} cleavage planes in chalcopryite (Figure 48c). With continuing enrichment, chalcopryite, bornite and covellite are successively replaced by medium grey whitish chalcocite, medium bluish grey chalcocite, darker grey chalcocite, and finally by medium dark grey chalcocite (Figure 48d) as seen with reflected light in
polished sections (Castro-Reino, pers. commun.). This general sequence is interrupted by renewed covellite enrichment after the development of the medium grey whitish chalcocite and after the development of the dark grey chalcocite, concurrently with the development of the late medium dark grey chalcocite. Marcasite appears to have replaced pyrrhotite during the development of the medium bluish grey chalcocite stage. Pyrite is replaced last in the sequence and is associated only with the medium dark grey chalcocite. XRD and microprobe analysis of similar samples indicate that medium dark grey chalcocite is classic chalcocite ($\text{Cu}_{2.00}\text{S}$), and that darker grey chalcocite is probably djurleite ($\text{Cu}_{1.96}\text{S}$), bluish grey chalcocite is probably anilite ($\text{Cu}_{1.75}\text{S}$), and the medium grey whitish chalcocite is probably an intermediate phase such as digenite ($\text{Cu}_{1.80}\text{S}$). This interpretation will require additional microprobe studies to confirm the mineralogy of the chalcocite phases. With that in mind, the overall supergene paragenetic sequence in the enrichment cycle would then be: cp, (bn) $\rightarrow$ bn/id or cov $\rightarrow$ dg $\rightarrow$ an $\rightarrow$ dj $\rightarrow$ cc, and py $\rightarrow$ cc.

The general paragenetic sequence in the leaching phase of supergene enrichment is relatively straightforward. In strongly leached samples hematite and goethite replace chalcocite and magnetite. In some weakly leached samples, covellite and dark blue chalcocite (?) replace earlier medium dark grey chalcocite following the reverse sequence of enrichment. No other intermediate chalcocite phases were observed in this sample set at Morenci; however, the presence of other phases such as those reported at Malanjkhand, India (Sikka et al., 1991) should be expected in the partially leached zone and at the top of the enrichment blanket. The non-uniform but widespread occurrence of covellite at the top
of the enrichment zone in the Morenci and Metcalf areas may be a reflection of the reverse sequence under continued oxidizing conditions.

Secondary Copper Oxide Mineralization

Copper oxide mineralization is highly variable and often contains multiple bands or layers of various copper oxide minerals. In addition, the great variety of local environments, and consequently local variations in chemistry, make it difficult to determine paragenetic relationships. With this in mind, however, the general paragenetic order appears to be chalcanthite → brochantite → tenorite → malachite → azurite → chrysocolla → copper-bearing clays. In some samples, azurite cross cuts malachite, which is then cross cut by chrysocolla that contains clasts of azurite (Melchiorre, pers. commun.). Moolick and Durek (1966) reported the frequent occurrence of chrysocolla as pseudomorphs after malachite and azurite. This general paragenetic sequence is not always in order. In places, malachite forms spectacular pseudomorphs after 0.5 to 1-cm sized azurite crystals, and in a few strongly oxidized zones, cuprite and native copper directly replace chalcocite.

Discussion

Interpretation of Morenci Leached Capping

The presence of iron-oxide mineralization and depleted copper contents of leached zones are the remnants of supergene processes that began in the Miocene and still continue today. Boxworks of hematite after chalcocite, and quartz after pyrite are common in
leached capping at Metcalf and elsewhere in the district. The hematite boxworks have been interpreted to represent the destruction of a pre-existing enriched blanket at Metcalf during Miocene to Pliocene time (Titley and Marozas, 1995; Titley and Enders, 1998; Moolick and Durek, 1966; Langton, 1973; North and Preece, 1993; Cook, 1994; Enders et al., 1998b). The partial leaching of the upper levels of the enriched blanket and in the relatively narrow, oxidized fractures that penetrate the enriched blanket is consistent with a drop in base level, as a result of down cutting of the Gila River during Pleistocene time (this study). Recent mining has exposed all of these zones and caused the water table to further drop in the Metcalf area because of pumping from sumps in the pit. Seeps and springs along faults and fractures above the current water table are accompanied by strong oxidation of chalcocite and pyrite in the enriched blanket. Oxidation has formed jarosite+/-goethite after pyrite, chalcanthite after chalcocite, and left goethite and hematite behind in the leached fractures and iron-hydroxides plus copper sulfates on the adjacent pit floor and walls. Microbiological and geological studies of the 5200 Bench at Metcalf have shown that acidophilic iron oxidizing bacteria play an important role in the leaching environment (see next chapter and Enders et al., 1998a). The active leaching visible today in the Metcalf area may have been the same process that produced the leached capping across the district since the mid-Miocene.

Lateral Transportation

Evidence for lateral transportation of copper in the Morenci district comes from several observations. This evidence includes the distribution of the relative degree of
enrichment (enrichment factor) and calculated eroded thicknesses across the district as discussed in previous sections. In addition, the Chase Creek graben contains most of the supergene mineralization in the district, and appears to have acted as a trap for supergene solutions as discussed in the following section. Field observations provide additional evidence, particularly at Northwest Extension.

The Las Terrazas fault was an important ore control at Northwest Extension, particularly during supergene mineralization, where it appears to have been the site of deposition of laterally transported copper. The fault contains angular to subrounded fragments of older granite porphyry and Proterozoic granite in a matrix-supported breccia, and gouge. In the oxide zone, the matrix is locally composed of malachite, azurite, and chrysocolla with fine, sharp-edged azurite crystals lining vugs within the gouge zone that indicate deposition after movement along the fault (North and Preece, 1993). Pseudomorphs of malachite after azurite are common. In the sulfide zone, the fault breccia contains fragments that contain chalcocite and covellite replacing chalcopyrite and pyrite. In cross section (Figure 42), the fault appears to localize oxide copper mineralization in the hanging wall, but it does not appear to significantly offset the enriched blanket. The blanket, however, contains widely different pyrite to chalcocite ratios across the Las Terrazas and Drumlin faults with values ranging from 6 to 10 in the footwall to 1.5 to 4 in the hanging wall (Figure 37). This offers a plausible explanation for the dominance of copper oxide mineralization resulting from in-situ oxidation of a former pyrite-poor enriched blanket in the hanging wall of the fault and thorough leaching of a pyrite-rich blanket in the footwall. In addition, the fault appears to control the location of high-grade
copper oxide and supergene sulfide mineralization relative to the surrounding hanging wall and footwall blocks without any significant effect on hypogene copper grades. This is indicative of favorable conditions for lateral transportation and deposition of copper in the fault during supergene mineralization.

Structural Control and the Role of Grabens at Morenci

Structures play a key role in determining the configuration of the enrichment profiles at several scales. The original stockwork fracture density is a control at a small scale, but it affects huge volumes of rock. At a larger scale, faults displace mineralization in response to episodic tectonism and channel flow. In the Morenci district, a system of faults created the Chase Creek graben, a large-scale feature that controls the distribution of supergene mineralization throughout the district (Figure 10). Multiple, stacked enriched blankets occur in parts of the Chase Creek graben in the Morenci, Western Copper, Northwest Extension, Metcalf, and Garfield areas.

All of these features played a prominent role in the formation of the thick, high-grade enrichment blanket in the Morenci pit area. To begin with, this area of the district contained some of the most extensive and highest grade hypogene mineralization with a high total sulfide content and pyrite-to-chalcopyrite ratios averaging >4. This mineralization occurred in a stockwork with a fracture density that averaged 0.9/cm or a parallel fracture spacing of 1.1 cm. In addition, the Morenci pit area contains the Apache, Copper Mountain, Niagara, Kingbolt and Quartzite fault zones that were responsible for ground preparation prior to enrichment, offsetting early cycle enrichment, and focusing
fluid flow through subsequent leaching and enrichment cycles. At a microscopic scale, the
cataclastic textures in samples from the enriched zone in drill hole #1193 (Figure 47c) are
evidence that enrichment and tectonism were concurrent. The result is a very complex
pattern of overprinting supergene zones.

Mineral profiles in the Chase Creek graben in the Morenci pit area exhibit multiple
stacked enrichment profiles. This is displayed in a simple example in drill hole #1193
(Figures 45 and 46b). In this profile chalcocite in the enriched zone overlies a well-
developed covellite + chalcopyrite zone in the middle and nascent blanket that overlies
low-grade hypogene, and a second, lower, poorly developed nascent enriched zone
containing chalcocite and chalcopyrite. More data are available on cross section 12,000N
that shows very complex enriched profiles (Figure 46). In this area of the Chase Creek
graben, the profiles show two or three stacked enrichment sequences. On either side of the
graben, the profiles display simple enriched sequences from leached capping into
enrichment down into hypogene at depth. Drill hole MO-2, in the center of the graben,
shows three sequences, each with partially developed or incomplete intermediate zones
that persist to a depth of 530 m (1,740 ft). The uppermost part of the sequence has been
partly destroyed by leaching (LC, PL, PLEZ$_3$) to a depth of 180 m (590 ft) below the pre-
mine surface. This sequence overprints the well-developed enriched blanket (EZ$_3$) that
forms the bulk of the deposit at Morenci. In places the enriched blanket contains well-
developed middle and nascent zones that persist to a depth of 300 m (1,000 ft). The
intermediate blanket (EZ$_2$) below contains a sequence in hole # MO-2 that includes an
enriched zone, nascent blanket and hypogene zone that extends to 460 m (1,510 ft) in depth.
The deepest blanket (NB$_1$) is poorly developed and contains chalcocite that replaces chalcopyrite and pyrite but without appreciable increases in total copper content. This deeper zone also occurs in drill hole MO-1 in the footwall of the Niagara fault.

The repeated, stacked enrichment profiles in the Chase Creek graben at Morenci were created by a complex sequence of erosion, chemical weathering, and structural deformation. The classic top-down model is that supergene enrichment is the result of progressive downward movement of the water table with time (Figure 6), and that repeated cycles are a result of structural offset after formation. In this model, differential uplift or base level drop continually exposes sulfides to the oxidizing environment where they are leached, and copper sulfates are transported to the water table where they replace and enrich chalcopyrite and pyrite. This process progresses through multiple cycles with each cycle further enriching and thickening the blanket. Alternatively, this same profile could be produced from the bottom-up as shown in Figure 50. In this model, initial enrichment produced a similar profile but where sulfides are only partially leached to form a first-cycle enriched blanket (Figure 50, panel A). This is followed by extension and graben formation with a sudden drop in base level (panel B). Base level recovery over time established a higher water table where a younger, second-cycle enriched blanket was formed by thorough leaching of the overlying sulfide-bearing partially leached zone (panel C). Continued graben deepening associated with crustal extension and the formation of the Duncan basin caused further base level drop. This exposed the second-cycle blanket to oxidation leaving hematite boxworks after chalcocite and a thicker and higher-grade third-cycle enriched blanket below (panel D). The final result was a composite enriched blanket
with multiple, stacked enrichment zones with widely variable sulfide mineralogies. The pronounced lateral enrichment at Morenci just added even more copper to be efficiently trapped in the graben.

Mass Balance Implications

The isopach map of calculated eroded thicknesses (Figure 39b) indicates that approximately 6.5 km$^3$ (1.5 mi$^3$) of rock must have been efficiently leached and eroded to account for all of the contained copper in the district. Assuming an average bulk density of 2.52 g/cm$^3$, this represents about 16 billion tons of rock. If the average grade were 0.16% Cu, this further represents about 26 million tons of copper or roughly 93% of the reported past production and known resources in the district (Table 1). The remaining 7% of the copper is from the remaining leached capping and partially leached zones, and in the original hypogene content of the profile, or was lost from the system.

The average calculated eroded thickness of 0.3 km (956 ft) is a minimum value because it is based on the assumption that 100% of the copper was leached out of the rock prior to erosion. This is probably an optimistic assumption. The average grade of copper in the remaining leached capping (Table 16) averages 0.08% Cu and ranges from 0.01% to 0.60% Cu (for small “perched” mineralized zones); however, the probability distribution shows that 70% of the composite values are <0.08% Cu. Drill hole data on cross sections throughout the deposit show that, in general, copper grade in the leached capping gradually increases with depth and that the zone contains discontinuous lenses and pods of higher grade sulfide and oxide mineralization. Additionally, the average grade of the hypogene
mineralization may be slightly overstated, based on the presence of supergene effects in Population 4 samples. In this case, the amount of eroded and leached material required would have been greater than initially calculated. Conversely, this could have been offset by higher grades in the overlying Paleozoic sedimentary rocks, which would require less eroded thicknesses. Calculated eroded thickness is a linear function of hypogene copper grade (Equation 6), and it is a simple exercise to estimate the order of magnitude of changes with different assumptions. For example, assuming a 50% leaching efficiency before erosion or average leached capping grade of 0.08% Cu, the calculated eroded thickness would still only be 0.6 km (1,900 ft) and the eroded volume would be approximately 13 km$^3$ (3 mi$^3$).

Estimates of depths of burial (see Initial Depth of Burial section) indicate that a minimum thickness of 1.7-1.9 km (5,580-6,230-ft) of rocks must have covered the deposit during its formation. This leaves at least 1.1 to 1.6 km (3,600 to 5,250 ft) of potentially mineralized rock unaccounted for in the geologic record. From regional stratigraphic evidence, it is permissible that the total Paleozoic and Mesozoic cover at the time of mineralization could have been from 1.8 (5,900 ft) to over 2.4 km (7,900 ft). Although it was permissible for enrichment to have occurred prior to Oligocene volcanic activity, there is no evidence preserved in the rocks to substantiate this interpretation. This conclusion begs the question of what happened to Morenci during the 25 million years between the time the deposit was formed and when late Oligocene volcanic rocks began to cover it? It is possible that some of the copper in the deposit was derived from pre-volcanic, Oligocene supergene enrichment, but that all of the evidence for those cycles has
been removed from the geologic record in the deposit. On the other hand, it is entirely possible that copper was chemically and mechanically weathered from the deposit prior to mid-Tertiary volcanism. In that case, the question is whether the geologic processes of concentration or dispersion dominated during the Oligocene? The presence of a north to north-east directed drainage system during the Eocene to early Oligocene and Laramide-age volcanic rocks in the rim gravels to the north in the Eocene Baca basin may indicate that the forces of dispersion were dominant.

These questions have a profound significance for exploration in the district. The lower conglomerate is the only pre-volcanic, Oligocene or Eocene sedimentary unit in the district; and unfortunately, where these rocks outcrop; they do not contain any evidence of mineralization or alteration. The answers probably lie deeply buried beneath volcanic cover to the north or below thick alluvial fill in the adjacent valleys, waiting to be discovered.
THE ROLE OF MICROORGANISMS IN THE SUPERGENE ENVIRONMENT
OF THE MORENCI PORPHYRY COPPER DEPOSIT

Introduction

The supergene environment occurs near the surface of the earth - that special place where the atmosphere, hydrosphere, and biosphere interact with the earth’s crust. As a result, it is reasonable to assume that each of these fundamental environmental spheres will exert some control over the processes that operate in this unique region of the planet. For the most part, traditional genetic models of supergene enrichment have followed an inorganic geochemical approach to ore forming processes. Work over the last several decades, however, has shown that iron-oxidizing bacteria play a fundamental role in the formation of acid mine drainage and that sulfate-reducing bacteria (SRB) can be effectively used to clean up some of those same sites. In addition, the widespread application of solvent extraction and electrowinning (SX/EW) technology to leaching low-grade copper deposits has heightened our understanding of the role that bacteria play in this process. Because these bacteria are naturally occurring microorganisms, the question is: what role have they played in the formation of supergene copper deposits?

The Metcalf deposit is an ideal location to study supergene processes. As described in the previous chapter, the 5200 Bench traverses a classic, but tilted, enrichment profile consisting of a 200-m (650-ft) thick zone of leached capping that overlies a partially leached, 180-m (590-ft) thick enriched blanket. Actively weathering zones along this bench provide a natural laboratory to study supergene processes. In
addition, exposures of “paleo-leaching and enrichment zones” are also available for study in core and in the pit.

This chapter has been taken from Enders et al., (in prep). Descriptions of the study site, geologic setting, and previous work at Morenci are included elsewhere in this dissertation, and are not repeated here. This chapter provides information about the geochemical and biochemical processes of leaching and enrichment in the supergene environment, and compliments the work described in the preceding chapters, with minor repetition.

Previous Work

Ehrlich (1998) provided a good summary of the role that microorganisms play in geologic processes. Rudolfs (1922) was the first to describe the oxidation of pyrite by “sulfur-oxidizing” organisms. Subsequently, Colmer and Hinkle (1947), Colmer et al. (1950), Bryner and Anderson (1957), and Nielsen and Beck (1972) described the role of iron-oxidizing bacteria in the formation of acid mine drainage from coal and metal mines and in leaching chalcocite and molybdenum ores. With the overall heightened environmental awareness that began in the 1970’s and the EPA’s concern with abandoned mine lands in particular, a fairly large volume of knowledge has accumulated regarding the environmental geochemistry of sulfide mine-wastes (Jambor and Blowes, 1994). In addition, the traditional boundaries between biology and geology have been blurred resulting in a comprehensive treatment of geomicrobiology by various workers notably Banfield and Nealson (1997). In particular, Nordstrom and Southam (1997) provided an
excellent review of the role of bacteria in sulfide mineral oxidation. Concurrent work in mine tailings environments and on remediation projects have provided new insights into the role of sulfate-reducing bacteria in biomineralization, metal and sulfur biocycling, and related biogeochemical phenomena (Dvorak et al., 1992; Hammack et al., 1994; Fortin et al., 1995, 1996, Fortin and Beveridge, 1997).

A wealth of information about the geochemistry and biochemistry of leaching is now available as results of work in the mining and hydrometallurgical fields since the 1960’s. Murr (1980) provided an excellent review of the theory and practice of copper sulfide dump and in-situ leaching. Work since then has provided additional insight into the chemistry, biology, kinetics, hydrodynamics, and mechanics of leaching which offer an alternative and complementary perspective from which to re-evaluate some of the classical notions of supergene processes. The literature covering those topics is too voluminous to recite in the context of this paper. Recent work from this body of literature (Sand et. al., 1995; Schippers et. al., 1996; Gehrke et. al., 1998; and Schippers and Sand, 1999), however, provides a more detailed understanding of the sulfur chemistry and bacterial leaching mechanisms that operate in the leaching environment, and provides an analogue for comparison to the natural environment.

Geologists have speculated for years about the role of bacteria in ore-forming processes. In fact, Lovering (1959) was the first to mention the “tremendous” magnitude of the chemical effect that soil biota could cause in general. Titley (1975) was the first to postulate a link between microorganisms and the rapid rates of copper leaching in some of the porphyry copper districts in the southwestern Pacific region, an area of high
precipitation and erosion rates. Alpers and Brimhall (1989) proposed bacterially mediated sulfate reduction as a mechanism to explain a thin zone of massive chalcocite at the top of the enrichment blanket at La Escondida, Chile. Lichtner and Biino (1992, p.4012) questioned the potential role of SRB in direct precipitation of pyrite, bornite, and chalcocite in enrichment blankets. More recently, Sillitoe, Folk and Saric (1996) proposed bacteria as mediators of copper sulfide enrichment based on a scanning electron microscope study of chalcocites from copper deposits in northern Chile. Enders et al. (1998a) were the first to report the actual occurrence of viable acidophilic iron oxidizing bacteria obtained from weathering outcrops of the Morenci porphyry copper deposit and propose a biochemical link with the classical geochemical aspects of supergene enrichment processes. The results of that original work and subsequent studies at Morenci are reported in this paper.

General Approach

This study was a collaborative effort between Phelps Dodge Morenci, Inc., the Department of Biosciences at Northern Arizona University, and the Department of Geosciences at The University of Arizona. The work was conducted in conjunction with other geological studies of the supergene environment at Morenci and involved four sampling events in two phases of work over a two-year period from November 1997 through November 1999. The first phase involved three sampling events: 1) to initially determine general background levels of *Thiobacillus ferrooxidans* in Morenci materials, 2) to further establish the existence of *T. ferrooxidans* within the deposit across a
supergene profile exposed on the Metcalf 5200 Bench, and 3) to confirm seasonal effects by re-sampling established sites. The second phase focussed on two objectives. The first objective was a small reconnaissance sampling of targeted environments for SRB that was conducted concurrently during the third field trip, and the second objective was a broader follow-up based on the reconnaissance results. The fourth sampling event was designed to re-sample existing *T. ferrooxidans* sites for SRB and expand the study to additional sites as mining progressed. In addition, geologic mapping, geochemical sampling, alunite-jarosite $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology, and sulfur isotopic studies were conducted along with thin section and polished section study to establish the geologic setting and mineralogical characteristics of the supergene environment and to provide context within which to interpret the results.

**Geology of the Metcalf Study Site**

Mining in the Metcalf area has exposed a classic, but tilted, enrichment profile (Figure 41) that is well displayed on the 5200 Bench along the south side of the Metcalf Pit, where many of the sample sites are located (Figure 51). Supergene mineralization and argillic alteration are superimposed on strongly fractured and quartz-sericite-pyrite altered Laramide-age monzonite porphyry and older granite porphyry, and Proterozoic granite (Figure 28). The War Eagle fault zone has both offset the enriched blanket and enhanced permeability along the zone resulting in a sharp transition from strong leached capping in the hanging wall to enriched sulfides in the footwall. The leached cap (sites J, H, and C) contains pervasive oxidation and a stockwork of quartz-hematite +/-goethite +/- jarosite
veins and veinlets left behind as a result of nearly complete leaching of the precursor pyrite and chalcocite mineralization. The enriched blanket (sites D, END, M, CNR, A, and B) contains disseminated pyrite and chalcocite mineralization in the matrix of the rock and a stockwork of 0.1 to 10 mm wide veins and veinlets of chalcocite, djurelite, and covellite that both coat and totally replace pyrite and chalcopyrite. In addition, very thin molybdenite veinlets crosscut the earlier quartz-sericite-pyrite-chalcocite veins. Late-stage, coarse–grained quartz-pyrite veins are also common throughout this part of the deposit.

The presence of iron-oxide mineralization and depleted copper contents of leached zones are the remnants of supergene processes that resumed in the Miocene and still continue today. Boxworks (Blanchard, 1968) of hematite after chalcocite, and quartz after pyrite are common throughout the leached capping along the 5200 Bench. The hematite boxworks have been interpreted to represent the destruction of a pre-existing enriched blanket at Metcalf during Miocene to Pliocene time (Titley and Marozas, 1995; Titley and Enders, 1997; Moolick and Durek, 1966; Langton, 1973; North and Preece, 1993; Cook, 1994; Enders et al., 1998b). Partial leaching (site CD) in the upper 90 meters of the enriched blanket has resulted in a rock mass that contains a mixture of hematite, goethite, and jarosite that partially to completely replace chalcocite and pyrite in places. Partial leaching is well displayed as relatively narrow, oxidized fractures (site G) that penetrate approximately 180 to 270 meters (590 to 885 ft) into the enriched blanket exposed on the east-side of the Metcalf Pit wall. This style of leaching is consistent with a drop in base level, as a result of down cutting of the Gila River during Pleistocene time. Recent mining
has exposed all of these zones and caused the water table to further drop in the Metcalf Pit area in response. Seeps and springs along faults and fractures above the current water table are accompanied by strong oxidation of chalcocite and pyrite in the enriched blanket. Oxidation (sites A and B) has formed jarosite +/- goethite after pyrite, chalcanthite after chalcocite, and left goethite and hematite behind in the leached fractures and iron-hydroxides plus copper sulfates on the adjacent pit floor and walls.

**Methods and Materials**

**Sampling**

A wide variety of materials were initially sampled to characterize background bacterial populations in the natural and mining environment before focusing on key exposures in the mine. Sample sites are shown on Figures 41 and 51 and listed in Table 17 relative to their position in the mineralized zone. Background characterization samples were taken on November 21, 1997 during the fall dry season. Background waters were sampled from the Morenci municipal water supply at the Geology Department drinking fountain and from injection water for core hole #2539. A total of 48 monitor wells were sampled for *T. ferrooxidans* from a network across the district. Samples were taken of both barren and pregnant leach solutions from the Central SX/EW facility. In addition, scrapings of core from drill hole #2539 and two outcrops (A, B) along the Metcalf 5200 bench were collected. Subsequently, seven additional sites were established along the Metcalf 5200 Bench (C, CD, D, END, CNR, G, and H) on February 20, 1998 during the winter wet-season. The third sampling event occurred on July 8, 1998 in the dry summer
season prior to the monsoons. All sites were re-sampled again. Two more sites were
established on the Metcalf 5200 Bench (J, M), and four additional sites were sampled in
the Metcalf Pit (MET-5000, MET-4900), Northwest Extension Pit (NWX), and the bottom
of the Morenci Pit (KB). In addition, six samples of tailings and pond water were
collected in the West Tailings Dam area. Three reconnaissance samples were collected
from the Morenci and Northwest Extension pits for SRB enumeration. The last sampling
was conducted almost one year later, on August 9, 1999 in the middle of the monsoon
season. Five new sites were established at new springs and seeps in Metcalf (4750-CNR,
4750-N, 4700-66, 4900-34B) and Northwest Extension (4200-A) to further expand the
coverage. Those sites plus five wet sites on the Metcalf 5200 Bench were sampled for
SRB. At each site, a corresponding sample of the wall rock was collected for
geochemistry and petrographic study, and five spring/seep samples were collected from the
wettest sites. Water samples were collected in clean, dry 1000-ml polypropylene bottles
and placed on ice for shipment to the lab. Sediment, rock scrapings, and water samples for
bacterial enumerations were collected in sterile 50-ml tissue culture tubes. Samples to
enumerate sulfate reducing bacteria were processed on-site due to the oxygen stress
associated with sampling while the thiobacilli samples were processed at Northern
Arizona University.

Geochemistry and Acid/Base Accounting

A total of 14 samples from the Metcalf 5200 Bench and Pit were submitted to SVL
Analytical Inc. in Kellogg, Idaho for geochemical analysis. The samples were analyzed for
total sulfur and soluble sulfur forms, and the acid generating and acid neutralization potentials of the samples were calculated. SVL used standard accepted industry and EPA analytical procedures as summarized in Jennings and Dollhopf (1995). In addition, splits of those 14 samples plus four more additional samples from the last sampling event were submitted to the Phelps Dodge Analytical Services laboratory in Morenci. The samples were analyzed for total copper, acid-soluble copper, molybdenum, ferric-soluble copper, iron, and total sulfur using standard analytical methods.

Site Hydrochemistry

The five samples of seep and spring waters were shipped to McKenzie Laboratories or Bolin Laboratory in Phoenix, Arizona for analysis. The samples were filtered and analyzed for pH, total dissolved solids (TDS), major cations and anions, nitrogen and nitrate-nitrite, phosphorous, sulfate, and alkalinity. In addition, the samples were analyzed for a Morenci-standard suite of dissolved metals (Sb, As, Be, Cd, Cr, Pb, Se, Al, Ba, Ca, Cu, Fe, Mg, Mn, Ni, K, Na, Zn, Hg, Ag, Tl). The samples were treated as if they were environmental monitoring samples with the appropriate sampling protocols and EPA test methods. Field pH and Eh were not measured during any of the four sampling events.

Enumeration of \textit{T. ferrooxidans} and Sulfate Reducing Bacteria (SRB)

The enumeration of \textit{T. ferrooxidans} and SRB were performed on liquid and ‘solid’ samples collected from acidic seeps flowing within the Morenci deposit. Laboratory pH
measurements were made directly on liquid samples. Solid sample pHs were measured after adding equal parts distilled water and sample material, vortexing for 1 minute, and allowing them to stand for 1 minute. *T. ferrooxidans* were enumerated by using the Most Probable Number (MPN) technique (Cochran, 1950) in a growth medium which consisted of 9K buffer, pH 2.3 (Silverman and Lundgren, 1959) containing 33.3 g/l FeSO₄•7H₂O.

Dissimilatory sulfate reducing bacteria were serially diluted in anaerobic saline (described below) and enumerated using the MPN method and the following chemically defined liquid culture medium (g/L): Bacto® Tryptone (10), MgSO₄•7H₂O (2), FeSO₄•7H₂O (0.5), Na₂SO₃ (0.5) and 60% sodium lactate (5.3 ml/l). The final solution was adjusted to pH 7.5 with 2N NaOH and filter sterilized. A reducing agent supplement (RAS, ascorbic acid [7.5 g/l] and thioglycollic acid [7.5 g/l], adjusted to pH 7.5 with 2N NaOH) was added to the medium at 10% (vol./vol.). Anaerobic saline (8-ml saline plus 1 ml RAS) was used for the serial dilutions.

The *T. ferrooxidans* and SRB cultures were grown at 25°C for 6 and 3 weeks, respectively to ensure that the end-point of growth had been reached.


Mineralogical polished thin sections were prepared using conventionally prepared mounts (Spectrum Petrographics Inc, Winston, OR) and examined by using reflected light (Ortholux petrographic microscope) and transmitted light microscopy (Nikon Labophot
photomicroscope). Wet mounts of SRB cultures were prepared by placing a 20 µl aliquot of culture onto a glass slide and placing a cover slip over the drop to spread the sample.

Samples for TEM were fixed with 1% (vol./vol.) glutaraldehyde, washed once using dH₂O, embedded in 2% low-melt agarose, dehydrated using a 100% acetone dehydration series and embedded in Epon 812 resin (Graham and Beveridge, 1990). Ultra-thin sections (70 nm) were cut using a Reichert-Jung® Ultracut E ultramicrotome, placed on Formvar-carbon coated 200-mesh copper grids and viewed unstained in a JEOL®-1200EX TEM.

Samples for SEM-EDS were applied directly to an aluminum SEM stub and allowed to dry under vacuum in the SEM chamber. EDS was performed using a Quantum Kevex® - 3300 light element detector attached to a LEO®-435VP SEM and quantified using a Kevex® software program to determine the relative proportions of Fe and S.

Sulfur Isotope Studies

Sulfur isotopes can be used to discern geochemical and biochemical characteristics of minerals. In particular, sulfur isotopes can be used to distinguish hypogene alunites from supergene alunites along with radiometric age dates, and field and petrographic relationships (Field, 1966; Field and Gustafson, 1976, Ohmoto and Rye, 1979). This approach has been successfully applied in a number of districts in conjunction with geochronology (Alpers and Brimhall, 1988; Cook, 1994; Sillitoe and McKee, 1996). Previous work described above indicates that sulfate in hypogene alunite tends to be fractionated with respect to hypogene sulfides resulting in δ³⁴S values of +8 per mil or
higher. In addition, supergene sulfates, including alunite and jarosite inherit sulfur from hypogene sulfides without significant isotopic fractionation, and retain their δ³⁴S values inherited from the sulfides ranging between −3 and +1 per mil in most porphyry systems (Ohmoto and Rye, 1979). Alternatively, bacterial sulfide-oxidation and sulfate-reduction at temperatures <50°C can result in significant sulfur isotope fractionation with values ranging from −2.5 to −46.0 per mil (Ohmoto and Rye, 1979; Hoefs, 1987; Brock et al., 1994; Ehrlich, 1998). Because of these characteristics, sulfur isotopes are useful for discriminating between geochemical and biogenic effects.

As an additional check on the field and petrographic work, the alunite and jarosite samples from the geochronology suite were submitted to three laboratories for sulfur isotopic analysis in three phases of work (Appendix B). The first phase was an orientation study of four jarosite and two alunite samples that were submitted to R.E. Rye for analysis at the U.S. Geological Survey Stable Isotope Laboratory in Denver. The second phase included the remaining alunites and jarosites, and samples of pyrite, chalcocite, and covellite from co-existing sulfides that were intermixed in four of the alunites. The second suite was sent to C.J. Eastoe for standard SO₂ sulfur isotope analysis in the Stable Isotope Laboratory in the Department of Geosciences at the University of Arizona following the methods of Robinson and Kusakabe (1975) and Coleman and Moore (1978). Sample #245 from the second suite yielded an anomalously low result at −20.5 per mil and was re-run to confirm the value (re-run −15.8 per mil). At this point, the potential to distinguish potentially biogenic sulfur isotopic signatures in supergene sulfides appeared worth pursuing. The published δ³⁴S values for supergene sulfides available for comparison
included only four samples (Field and Gustafson, 1976; Cook, 1994). Therefore, a third phase of work was initiated to determine the sulfur isotopic character of 13 more samples from representative supergene profiles at Morenci and 19 samples from porphyry copper deposits around the world. Clean, mono-mineralogical samples were submitted to C.J. Eastoe for analysis. The remaining samples contained fine mixtures of coatings and replacements of pyrite and chalcopyrite by secondary sulfides not very amenable to standard SO₂ sulfur isotopic analysis. These samples were submitted to F. Mazdab and prepared for microprobe analysis at the University of Arizona and for ion microprobe analysis using secondary ion mass spectrometry (SIMS) at Arizona State University in Tempe.

Alunite-Jarosite $^{40}$Ar/$^{39}$Ar Geochronology

Alunite \([\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]\) and jarosite \([\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]\) contain potassium and are therefore amenable to dating using K-Ar and $^{40}$Ar/$^{39}$Ar methods. As part of a related study of supergene enrichment (this study), a suite of 19 samples of alunite and 4 samples of jarosite were collected from representative supergene profiles in the Morenci district. Mineral separates were handpicked from the vein material and submitted to the Department of Geosciences X-ray Diffraction Laboratory to confirm the mineralogy. Clean samples were chosen for $^{40}$Ar/$^{39}$Ar dating at the New Mexico Geochronological Research Laboratory (NMGRL) at the New Mexico Bureau of Mines and Mineral Resources in Socorro (Peters, 1999c).
Results

Orientation Studies

The results from the initial orientation study established background characteristics and bacterial populations for a variety of materials. Samples of the incoming Morenci water supply, drilling water and a scraping of core from below the water table showed near-neutral pH” and no viable T. ferrooxidans (Table 18). Overall, pHs were also near neutral and no viable T. ferrooxidans were detected in the up-gradient groundwater monitor wells around the district (Table 18). In some of the down-gradient water wells in the Chase Creek stockpile and Tailings Dam areas, however, viable T. ferrooxidans populations were present in low concentrations ranging from $10^0$ to $10^1$ per ml in waters with neutral pH. As expected, bacterial populations in process solutions and solids were several orders of magnitude greater than background levels and ranged between $10^2$ to over $10^6$ per ml in materials with pHs between 1.4 and 2.8 (Table 19).

Seeps, springs and rocks from five of the most accessible sites in three of the mine areas were also sampled during the initial orientation survey. Background bacterial populations at these sites ranged up to $10^5$ per ml and were associated with acidic conditions that ranged from pHs of 2.1 to 5.4 (Table 20). The only sample without detectable T. ferrooxidans was from a puddle of rainwater in the Northwest Extension pit. In addition, one sample of grey mud from a seep at the bottom of the Morenci pit contained detectable SRB. Rock scrapings from Site B on the Metcalf 5200 bench contained $8.2 \times 10^3$ viable T. ferrooxidans per ml with a sample pH of 2.8, which was comparable to the values in the tailings samples (Table 19). The seeps, springs and rocks that were sampled
in the Metcalf area occur along fractures in the vadose zone, just above the water table, in an actively weathering sulfide bearing enriched zone. The results of the orientation survey showed that *T. ferrooxidans* occurred widely throughout the district, SRB were present in at least one location, and that the Metcalf area would be a good location for follow-up studies.

Populations of *T. ferrooxidans* and SRB at Metcalf

*T. ferrooxidans* and SRB enumeration results are presented in Table 21 and summarized in Figures 52, 53, and 54. These results are briefly described below.

*T. ferrooxidans* populations: Populations of viable *T. ferrooxidans* ranged from less than detection (0.18 MPN/ml) up to $3.50 \times 10^7$ MPN/ml during the two-year study. Table 21 shows the results from the four sampling events for all study sites. Figure 52 shows the average populations found at each site along the Metcalf 5200 bench over the study period. Although the data are not shown to scale across the figure, the sample sites are in the same order as they appear on the cross section in Figure 41. There were no detectable *T. ferrooxidans* at any of the sites in leached capping (sites H, C) or in the partially leached zone at the top of the enriched blanket (site CD). Populations increased almost six orders of magnitude in the enriched blanket (sites D, END, M, A, B) and were still present in the partially leached fracture zone at site G. Interestingly, no viable *T. ferrooxidans* were recovered from site CNR during the two sampling events. Rocks at this site contained pyrite in the groundmass, but none in veins or on open fracture surfaces.
**Seasonal effects:** Sample pH and *T. ferrooxidans* populations showed significant seasonality effects. Sampling events for this study coincided with one wet season (20 Feb 98), two dry seasons (21 Nov 97, 08 Jul 98) and one abnormally wet summer monsoon season (09 Aug 99) as shown in Figure 5. The seasonal variations of sample pH and *T. ferrooxidans* populations at each site along the Metcalf 5200 bench are plotted on Figures 53 and 54, respectively. All of the sample pHs were near neutral to acidic, but the dry season pHs were significantly lower than during the wet season at each site. In addition, the seasonal variation is significantly more pronounced in the enriched blanket (sites END, M, CNR, A, B, G) than in the leached capping and upper partially leached zone (sites H, C, CD), which indicates both a dilution as well as a biogenic effect. A similar pattern occurs in the *T. ferrooxidans* populations, where the bacteria thrive during wet periods, but the populations drop off several orders of magnitude during the dry seasons, presumably due to low water activity.

**SRB populations:** Populations of viable SRB averaged almost 500 MPN/ml at 11 of the 12 sites sampled during the fourth event and only one site (END) did not contain detectable populations (Table 21). SRB populations on the order of $10^2$ MPN/ml were found co-existing with *T. ferrooxidans* populations on the order of $10^2$ to $10^7$ MPN/ml for those sites with both data sets (Figure 52). Interestingly, the site with the highest number of *T. ferrooxidans* (4900-34B) also had the highest SRB population.
Site Conditions and Geochemistry

Site conditions, sample geochemistry, and sample character are summarized in Tables 22 through 25. The results are briefly described below.

**Seeps and springs**: The geochemistry of the five seeps and springs in the mine area associated with the sample sites is typical of acid mine drainage (Table 22). Average pH values were acidic and ranged from 2.6 to 4.6. These waters were significantly different than the typical groundwater in monitoring wells around the district. These seeps and springs contain copper-sulfate waters (copper = 248 mg/l, sulfate = 2108 mg/l), have no detectable alkalinity, contain elevated metal contents, and are all associated with significant populations of *T. ferrooxidans* (Tables 21 and 22). The seep at Site B along the Metcalf 5200 bench had the highest copper content (960 mg/l), the highest sulfate content (4,300 mg/l), and consistently high bacterial populations. Overall, copper concentrations were higher than iron, but locally the metal ratios were highly variable.

**Sample Geochemistry**: Laboratory tests on sulfur speciation and acid-base accounting showed that the wall rocks in the deposit have high acid generating potential and no acid neutralization potential as shown in Table 23. Exclusive of samples in the leached capping, sulfide sulfur contents comprised an average of 65% of the total sulfur content in the rocks and ranged from about 0.1% to over 8% S$_{sulfide}$ dominantly in pyrite and chalcocite (Table 24). Copper contents of the samples varied widely from <0.01% Cu in the leached capping to over 10% Cu in veins, and averaged about 0.52% Cu overall in the enriched blanket (Table 25). With the exception of site CNR, all samples in the enriched blanket contained pyrite and chalcocite in veins and along fracture surfaces. All
of the sample sites contained wall rocks composed of strongly altered older granite porphyry, Proterozoic granite or monzonite porphyry. These rocks contained pervasive quartz-sericite replacement of the original feldspars ranging from 5 to 40% of the matrix of the rock and 100% of the vein and fracture selvages (Table 24), and therefore, had no buffering capacity for acidic solutions.


TEM observations of unstained ultra-thin sections and transmitted light microscopy of culture mounts revealed the presence of abundant viable bacteria in samples from the actively weathering sites in the Morenci district. Figure 55 shows a photomicrograph of a culture of \emph{T. ferrooxidans} from site B. In this sample the bacteria are considered to be ‘healthy’, because they are non-mineralized, and are typical of acidophilic iron oxidizing bacteria in other acid mine drainage systems. SEM-EDS analysis of the dark fibrous minerals in the TEM image (Figure 55) indicated these minerals were jarosite (\(\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6\))

Transmitted and reflected light microscopy of sample #245 from the Metcalf pit revealed the possible presence of mineralized fossil SRB (Figure 56). Sample #245 was collected from a muck pile in the partially leached zone on the Metcalf 4800 bench approximately 95 meters (310 ft) below the pre-mine topographic surface and 35 meters (115 ft) above the enriched blanket. The sample contains a 1-cm wide alunite vein in strong quartz-sericite-pyrite altered Older granite porphyry. At a hand-scale, the rock
contains small 0.1 mm blebs of chalcocite replacements of pyrite and a grey ‘dusting’ of fine chalcocite in a lacy fringe along quartz/alunite grain boundaries and around 0.5- to 1-cm fragments of broken and re-healed alunite. At progressively higher magnifications in reflected light, the texture appears to be a fine mesh of dendritic aggregates of granules that are very uniform in size (Figure 56). In a transmitted light photomicrograph, the dark grains are 1-2 µm rod-shaped minerals that appear to be bacteria-sized and occur in clusters of cells (presumably microcolonies) (Figure 57a). These mineral morphologies are comparable to the bacteria-mineral assemblages that are produced by SRB grown in vitro. Transmitted light microscopy of cultured SRB from Morenci (Figure 57b) reveals 1-2 µm curved (vibriod)-shaped *Desulfovibrio* ssp. and larger, 2-4 µm rod-shaped *Desulfotomaculum* ssp. Microprobe analysis of sample #245 revealed that the coarser grained copper sulfide particles have a composition of Cu$_{1.87}$S. Because there is no known copper sulfide mineral with this composition, it is possible that the mineral may be a mixture of two or more copper sulfides such as digenite and djurleite.

**Sulfur Isotope Studies**

Sulfur isotope studies revealed that the chalcocite in sample #245 has an anomalously light δ$^{34}$S (-22.4 per mil) signature relative to other supergene and hypogene sulfides (Figure 58). For example, sulfur isotopic analyses of the 12 available samples of supergene chalcocite, djurleite, and covellite, and the co-existing pyrite in some samples, from the Morenci, Chino and Tyrone porphyry copper deposits in southeastern Arizona and southwestern New Mexico average –1.7 +/-1.0 per mil δ$^{34}$S (Tables 26 and 27). Overall,
these values are slightly lighter than the corresponding jarosites (-0.2 per mil) and alunites (+1.1 per mil) from the same samples as shown in Figure 58 (see following chapter). Sample #245, however, contained anomalously light $\delta^{34}$S values at -20.5 and -15.8 per mil, that are almost one order of magnitude lower than the other sulfides, which are consistent with biogenic sulfur fractionation.

Alunite-Jarosite $^{40}$Ar/$^{39}$Ar Geochronology

XRD and microprobe studies of sample #245 indicated that the sample contained too much kaolinite contamination to be a good candidate for $^{40}$Ar/$^{39}$Ar dating. Results from four nearby alunite samples yielded a range of ages from 7.0 to 11.0 Ma (see following chapter). Therefore, the fossil SRB encapsulated in the alunite from sample #245 are late Miocene in age and were formed during the most important period of supergene enrichment in the Morenci district (see following chapter).

Discussion

Microbiological and geological examination of the Metcalf area reveals that acidophilic iron-oxidizing and sulfate-reducing bacteria (SRB) have contributed to leaching and enrichment of copper in the supergene environment in the Morenci district. Here we propose a link between the geochemical and biochemical processes of leaching and enrichment in the supergene environment and suggest conditions in which one or the other dominates. We then take a look at the associated carbon budget and its implications
for bacterial sulfate reduction in the enriched blanket and for the formation of copper carbonate minerals in the partially leached zone.

Leaching

Chemical weathering of porphyry copper deposits begins when typically low-grade (0.05% to 0.35% Cu) primary pyrite and chalcopyrite mineralization are exposed to oxygenated groundwaters. To be efficient, this process typically requires pyrite-to-chalcopyrite contents >3:1 and total sulfide contents >4 wt.% (Titley and Marozas, 1995), and rocks low in feldspar and carbonate. In this case, oxidation of pyrite in the vadose zone and capillary fringe above the water table forms sulfuric acid and ferric sulfate that react with chalcopyrite to form soluble cupric sulfate and ferrous sulfate. The Eh and pH conditions under which this occurs are shown in Figure 59. This process leaves behind a “leached capping” that is typically devoid of copper and contains a mixture of the iron oxide minerals hematite, goethite, and jarosite which comprise the classic limonite assemblage (Blanchard, 1968; J.A. Anderson, 1982). Where this process is incomplete, a zone of “partial leaching” is left behind beneath the leached capping. This process is cyclical and reflects episodic downward changes in the position of the redox boundary as a result of tectonic, physiographic, and climatic changes (Figure 6). Subsequent cycles of erosion and weathering continue to dissolve copper minerals above the water table and both enrich and thicken the blanket with time (Brimhall et al., 1985). Where there is sufficient pyrite remaining, dissolution of pyrite and chalcocite in a former enriched blanket leaves behind a mixture of transported hematite and goethite, or a classic and
distinctive hematite boxwork (Titley and Marozas, 1995; J.A. Anderson, 1982). Although these processes are manifestations of inorganic geochemical reactions, acidophilic iron oxidizing bacteria play a significant role in catalyzing these reactions as discussed below.

**Geochemical processes:** Early cycle enrichment involves the oxidation and dissolution of pyrite and chalcopyrite. Transportation of copper in this environment is only possible under conditions of sustained low pH caused by the oxidation of excess pyrite. Stokes (1906) and Blanchard (1968) provided typical reactions in this environment that are shown in reactions (1) through (4) below.

1. **Atmospheric oxidation of chalcopyrite**
   \[
   12\text{CuFeS}_2 + 51\text{O}_2 \rightarrow 12\text{CuSO}_4 + 4\text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}_3\text{O}_3
   \]

2. **Oxidation and dissolution of pyrite**
   \[
   8\text{FeS}_2 + 28\text{O}_2 + 8\text{H}_2\text{O} \rightarrow 8\text{FeSO}_4 + 8\text{H}_2\text{SO}_4
   \]

3. **Oxidation of ferrous sulfate to ferric sulfate**
   \[
   8\text{FeSO}_4 + 4\text{H}_2\text{SO}_4 + 2\text{O}_2 \rightarrow 4\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}
   \]

4. **Dissolution of chalcopyrite**
   \[
   2\text{CuFeS}_2 + 4\text{Fe}_2(\text{SO}_4)_3 \rightarrow 2\text{CuSO}_4 + 10\text{FeSO}_4 + 4\text{S}^0
   \]

The ultimate result of reactions (2), (3) and (4) is the formation of 1 mol of chalcocite (Cu$_2$S) in the enrichment zone at depth (Titley and Marozas, 1995) as discussed in the Enrichment section below. Ferric sulfate leaching of chalcopyrite at temperatures <200°C directly or by bacterially catalyzed reactions, however, is slow and incomplete because of
its tendency for surface passivation (Hackl et al., 1995). Thus first cycle leaching and enrichment is relatively inefficient if erosion rates exceed chemical weathering rates.

Subsequent cycles of leaching and enrichment are much faster and involve the oxidation and dissolution of chalcocite and any remaining pyrite and chalcopyrite. Seep and spring water analyses in the Morenci district indicate there is abundant sulfate, copper, iron, and H+ in solution in the actively weathering zones (Table 22), and dissolution of chalcocite can occur by several mechanisms depending on environmental conditions. At acid pH, ferric iron is the most important oxidant for pyrite. At neutral or alkaline pH, however, oxygen is the important oxidant because of the low solubility of ferric iron above pH 3.5 (Sand et al., 1995). Ferric dissolution of chalcocite is a two-step electrochemical process where the first copper dissolution (rxn. 5) is very fast, but the second (rxn. 6) is very slow (Sullivan, 1930, 1931).

\[
\begin{align*}
(5) \quad \text{Cu}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{CuSO}_4 + \text{CuS} + 2\text{FeSO}_4 \\
(6) \quad \text{CuS} + \text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{CuSO}_4 + 2\text{FeSO}_4
\end{align*}
\]

Alternatively, chalcocite and covellite dissolution can occur through acid attack under oxidizing conditions as shown in equations (7) and (8). The absence of covellite in the actively weathering benches at Metcalf indicate that chalcocite dissolution in this environment may proceed directly to copper sulfate by equation (7) or by acid dissolution (rxn. 8) of intermediate covellite phases formed in equation (5).
The abundance of hypogene sericite and supergene argillic alteration takes most of the buffering capacity out of the rock as shown in the acid-base accounting tests (Table 23). This would drive reactions (7) and (8) to completion if there were enough acid available from dissolution of excess pyrite.

**Biochemical processes:** Acidophilic iron oxidizing bacteria significantly enhance metal sulfide dissolution by catalyzing leaching reactions like those described above. The most important of these bacteria are *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, with additional help from *Thiobacillus thiooxidans* (Colmer et al, 1950; Sand et al., 1995). The growth medium used for enumerating acidophilic iron oxidizing bacteria in this study resulted in the growth of *T. ferrooxidans*, which are by far the most significant bacteria in process solutions in the Morenci district (Uhrie, pers. commun). The bacteria studied at Metcalf were both abundant and healthy. For comparison, in metal-stressed environments downstream from acid mine drainage systems the bacteria are typically dead and mineralized (Southam et al., 1994). In these systems, the bacteria are associated with authigenic iron hydroxide precipitates (data not shown).

Biological oxidation requires an acidic pH (Colmer et al, 1950; Hallmann et al., 1993), the presence of oxygen and carbon dioxide, and humidity (Hallmann et al., 1993). Although one of the optimal conditions for growth of *Thiobacillus* spp. is pH <3 (Trafford et al., 1973; Amaro et al., 1991), colonization of sulfide minerals and resulting
chemolithotrophy is possible under 'neutral' pH conditions. This presumably occurs through the development of an acidic interface between the bacteria and the mineral surfaces (Southam et al., 1994). Cells grown on ore are difficult to dissociate from the ore particles (Gormley and Duncan, 1974; Suzuki et al., 1990; Southam and Beveridge, 1992) demonstrating that a tight “bonding” occurs between *Thiobacillus* spp. and the mineral surfaces. Strong adherence of *T. ferrooxidans* to minerals via iron precipitates (Southam and Beveridge, 1992, 1993) may have an important ecological role in reducing the diffusion of metabolic products (e.g., Fe$^{3+}$ and sulfuric acid) away from the cell-mineral interface. This would help maintain an acidic microenvironment at the mineral surface, and provide a potential source of soluble ferrous iron through repeated chemical oxidation of the sulfide thereby promoting the growth of *T. ferrooxidans* (Singer and Stumm, 1970; Wiersma and Rimstidt, 1984). Viable thiobacilli were present throughout the actively weathering fractures at Metcalf in populations exceeding $10^6$/g material at pHs up to 7.2 (Table 21).

*T. ferrooxidans* catalyze leaching reactions by oxidizing pyrite and converting ferrous ion to ferric ion. This is an indirect leaching mechanism and occurs when the bacteria attach and grow on the surface of a sulfide mineral as shown in Figure 60 (Sand et al, 1995). In detail, ferric ion in the form of a hexahydrate ion is the first agent to attack pyrite, and the first resulting sulfur component is thiosulfate (Sand et al., 1995). In general, however, this process can be described by the following reactions (modified from Singer and Stumm 1970):
(9) \( \text{FeS}_2 + \frac{7}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \)

(10) \( 2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \xrightarrow{\text{thiobacilli}} 2\text{Fe}^{3+} + \text{H}_2\text{O} \)

(11) \( 14\text{Fe}^{3+} + \text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \)

Reaction (9) is the same as reaction (2) above and is the initial inorganic weathering reaction when pyrite is exposed to oxygenated waters. \( T. \text{ferrooxidans} \) in the weathering environment then rapidly oxidize \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \) (rxn. 10) which is available to oxidize additional pyrite (rxn. 11). This regenerates additional \( \text{Fe}^{2+} \) for thiobacilli and establishes a propagation cycle between the iron oxidizing bacteria, dissolution of sulfide minerals, and the formation of metal-rich sulfuric acid leachates (Fortin et al., 1995). Not only is the \( \text{Fe}^{3+} \) available to leach pyrite, it is also available to leach chalcopyrite, chalcocite, and covellite as in reactions (4), (5) and (6). Furthermore, the excess \( \text{H}_2\text{SO}_4 \) in reaction (11) can react with chalcocite and covellite as in reactions (7) and (8) or with the wall rock in silicate alteration reactions.

Chemical attack of the sericite-bearing wall rocks during these processes results in the formation of jarosite, alunite and kaolinite in the actively weathering zone as shown in reactions (12), (13) and (14).

(12) Formation of jarosite and kaolinite

\[
2\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 6\text{FeSO}_4 + 12\text{H}_2\text{O} + 3/2\text{O}_2 \rightarrow \\
\rightarrow 2\text{KFe}_3(\text{SO}_4)_{2}(\text{OH})_6 + \text{Al}_2\text{Si}_5(\text{OH})_4 + \text{H}_2\text{SO}_4
\]
(13) Formation of alunite

\[ 2\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow \]

\[ \rightarrow 2\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{SiO}_2 \]

(14) Formation of kaolinite

\[ 2\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 2\text{H}^+ + 3\text{H}_2\text{O} \rightarrow 3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ \]

The kaolinite tends to retain moisture, which promotes bacterial growth. Thus the moist mixture of chalcanthite, jarosite, ferrihydrite and kaolinite that occurs along the actively weathering fractures in the Metcalf 5200 bench can be thought of as a biochemical wedge of leaching. Once the sulfides have been oxidized, all of the copper and some of the kaolinite appear to be flushed from the fractures that leaves a quartz + goethite +/- hematite secondary mineral complex.

Enrichment

The available information indicates that inorganic geochemical processes dominate supergene enrichment. In certain environments, however, it appears that low-temperature biogenic sulfate reduction can directly precipitate secondary copper sulfides. These two processes are described and related below.

Geochemical processes: Classic inorganic geochemistry of enrichment is the process whereby copper is transported as an acid sulfate solution downward to the redox boundary at or below the water table where it reacts with the reduced sulfur in chalcopyrite and pyrite and forms secondary copper sulfides in an “enriched blanket”. The
resulting phase relationships are shown on the Eh – pH diagram for the copper species in Figure 59b. These relationships indicate that enrichment can occur through an increase in pH or a decrease in Eh over a wide range of acidic pHs so long as the Eh is less than 0.4 to 0.0 mV. Downward zoning of secondary copper sulfides reflects changing redox conditions and solution chemistry which yields a suite of secondary copper minerals with variable copper to sulfur ratios ranging from chalcocite (Cu$_{2.00}$S), djurileite (Cu$_{1.96}$S), and digenite (Cu$_{1.80}$S), anilite (Cu$_{1.75}$S), to covellite (Cu$_{1.00}$S). Secondary sulfide minerals follow the Schurmann’s Series (Lindgren, 1933; Schurmann, 1888) where copper preferentially replaces sphalerite before chalcopyrite, and chalcopyrite before pyrite. Replacement textures range from complete replacement to thin coatings on grain boundaries.

Enrichment appears to be a two-step process, where base metal cation exchange converts the sulfides to covellite. Then, in the presence of excess copper sulfate and continuing reducing conditions, covellite is reduced to form one of the chalcocite family of secondary copper sulfides. Replacement of pyrite is actually an acid generating process, and neutralization reactions such as argillic alteration of silicates actually promotes further enrichment. These reactions are shown in equations (15), (16), (17) and (18) (after Blanchard, 1968) below:

\[
(15) \quad \text{Replacement of sphalerite} \\
\text{ZnS} + \text{CuSO}_4 = \text{CuS} + \text{ZnSO}_4
\]
(16) Replacement of chalcopyrite

\[ CuFeS_2 + CuSO_4 = 2CuS + FeSO_4 \]

(17) Replacement of pyrite

\[ 4FeS_2 + 7CuSO_4 + 4H_2O = 7CuS + 4FeSO_4 + 4H_2SO_4 \], and

\[ 5FeS_2 + 14CuSO_4 + 12H_2O = 7CuS + 5FeSO_4 + 12H_2SO_4 \]

(18) Reduction of covellite to chalcocite

\[ CuS + CuSO_4 + H_2O = Cu_2S + H_2SO_4 + \frac{1}{2}O_2 \]

**Biochemical processes:** The presence of micro-fossilized (mineralized) SRB in sample #245 with an isotopically light biogenic $\delta^{34}S$ value, and large populations of viable SRB in the actively weathering environment at Morenci demand a somewhat different explanation. It is proposed here that in certain supergene environments, SRB can directly precipitate secondary copper sulfide minerals through sulfate reduction. Although this mechanism has been speculated to occur in some supergene environments (Alpers and Brimhall, 1989; Lichtner and Biino, 1992), the discovery at Morenci is the first physical evidence of direct sulfate reduction in a porphyry copper deposit. This mechanism is not unusual in similar environments. For example, low-temperature (~25°C) biogenic sulfate reduction and the formation of diagenetic copper-bearing Fe sulfides has been reported in tailings at Kidd Creek (Fortin and Beveridge, 1997). On another front, a CuS-$S^0$ concentrate with 33% Cu has been produced in bench-scale experiments from metal mine drainage at the abandoned Rio Tinto copper mine in Nevada using a low-temperature SRB sludge blanket bioreactor (Hammack et al., 1994).
Iron sulfide is the most common metal sulfide precipitate attributed to biogenic activity (Bubela and McDonald, 1969; Trudinger, et al., 1985); and by analogy, it is a process similar to biogenically precipitated copper sulfides. A core prerequisite of biogenically formed sulfide is the presence of organic carbon and sulfate. The basic biochemical and geochemical reactions mediated by dissimilatory sulfate-reducing bacteria (SRB) (Tuttle et al., 1969) are shown in equations (19) and (20) below:

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-
\]

\[
\text{M}^{2+} + \text{H}_2\text{S} \rightarrow \text{MS}_{(s)} + 2\text{H}^+
\]

(where M\text{\textsuperscript{2+}} represents a divalent metal ion such as Fe\text{\textsuperscript{2+}} or Cu\text{\textsuperscript{2+}})

In the Morenci supergene system, the source of organic carbon is presumably from the fixation of CO\textsubscript{2} within the overlying weathering profile by thiobacilli (Fortin et al., 1995, Fortin and Beveridge, 1997). During the wet season the thiobacilli flourish, in part due the meteoric input of dissolved oxygen, fixing carbon into the supergene system. During the dry season, thiobacilli, which do not possess a resting stage, die releasing organic carbon. Subsequent wet seasons wash this organic carbon down into more favorable redox conditions for bacterial sulfate reduction and promote the beginning of another cycle of carbon fixation (see Leaching section above). The presence of SRB in such a low pH environment has been described in acidic mine tailings systems (Fortin et al., 1995) so it is not surprising to find SRB activity associated with a supergene system.
The unusual aspect of the SRB mineralization observed at Morenci is the precipitation of covellite or chalcocite as opposed to pyrite. The reason that bacterial pyrite formation did not occur is the same as that ascribed to sulfide replacement. According to the Schurmann’s Series, copper has a lower solubility and will precipitate first if both FeSO₄ and CuSO₄ are present. Once biogenically precipitated covellite is formed, it can be reduced to one of the chalcocite family of copper sulfides during diagenesis, according to reaction (18) above.

At Morenci, the redox boundary can be spread over 10’s of meters allowing for a high probability of low redox microenvironments to support SRB activity. In this case, we would expect to see biogenic copper sulfides at the top of the enrichment profiles as in sample #245 at Morenci or in the massive chalcocite at the top of La Escondida (Alpers and Brimhall, 1989). Admittedly the database is small, and biogenic chalcocite appears in only one of the seven samples with sulfur isotopic data available to-date. Evidence from replacement textures from most everywhere else at Morenci, however, indicates that the texture in sample #245 is very unusual, and it would appear that geochemical non-biogenic processes account for most of the observed supergene enrichment. It is also possible that unless the mineralized bacteria are encapsulated in alunite or silica, the copper sulfides may re-crystallize and lose their bacterial integrity. In that case, the only trace would be the biogenic isotopic signature of the secondary copper sulfides formed by bacterially mediated sulfate reduction.
Estimation of the Carbon Budget in the Supergene Environment

Order of magnitude estimates of the carbon budget indicate that there is ample organic carbon available to support supergene processes. The estimates can be made using the mass of *Escherichia coli* (3x10^{-13} g dry weight, Neidhardt et al., 1990) as a proxy for *Thiobacillus* spp., which is similar in size (Kelly and Harrison, 1984). The most active seep along the Metcalf 5200 bench (site B) has on the order of 10^7 cells/g (Table 21). This would yield about 3x10^{-6} g of organic carbon (CH_2O, 40-wt.% C) per gram of material or 1.2x10^{-6} g of organic carbon per gram of fracture material. Typical fracture densities in the highly mineralized areas are about 0.4/cm (length/area) which is a fracture spacing of 2.5 cm. At this average spacing, a 100-m x 100-m x 100-m block of this material would contain about 3.8 vol.% fractures if the average fracture width is 0.1 cm

[(0.1cm/2.6cm)*100] for a total volume of 3.8x10^9 cm^3 of fractures. At an average bulk density of 2.5 g/cm^3, the 100-m x 100-m x 100-m block would contain 1.1x10^1 tons of organic carbon. This renewable inventory would be periodically flushed from the system and transported to the water table at depth where it would be available for SRB growth.

Melchiorre and Enders (in prep) are suggesting that oxidized carbon from residual, dead *T. ferrooxidans* contribute to the light carbon isotopic signature of azurite in the oxide zone at Northwest Extension. If this same 100-m x 100-m x 100-m block had an average grade of 0.25% Cu as azurite, the block would contain 6.25x10^3 tons of copper or 11.3x10^3 tons of azurite (55.3 wt.% Cu). Azurite contains 7.0 wt.% carbon, so the example block would contain about 7.9x10^2 tons of carbon. The instantaneous organic carbon inventory calculated above would account for 0.014% of this total. Given the estimated 10,000-
100,000-year time spans for leaching (Ague and Brimhall, 1989; Lichtner and Biino, 1992), it is not unreasonable for subsurface bacterial carbon to comprise a significant proportion of the carbonate in azurite.

**Conclusions**

The results of this geological and microbiological study in the Morenci district strongly indicate that microorganisms play a fundamental role in the formation of supergene enrichment. It is clear that acidophilic iron oxidizing bacteria like *T. ferrooxidans* catalyze a number of geochemical reactions in the weathering environment that leach copper out of the oxidized zone above the water table. Although the predominance of evidence indicates that the enrichment process proceeds via geochemical reactions, in some environments dissimilatory sulfate reducing bacteria (SRB) appear to contribute to enrichment by directly precipitating chalcocite from solution through bacterial sulfate reduction. Evidence for these processes can be observed today in actively weathering environments and in the geologic record in the leached capping, partially leached zones, and enriched blanket at Metcalf. K-Ar dating of alunite in the supergene profile at Morenci indicates that fossil SRB were active during the Miocene.

Supergene ore forming processes are thus the result of both biochemical and geochemical reactions. These reactions are linked through a series of cycles involving water, oxygen, carbon dioxide, iron, sulfur, and copper near the surface of the earth where the atmosphere, hydrosphere, and biosphere interact with the earth’s crust (Figure 61). Supergene processes begin in the vadose zone above the water table when *T. ferrooxidans*
in the soil and rock near the earth’s surface interact with the mineralized interface of an eroding copper deposit. Chemical weathering below the water table is limited by oxygen content, and the oxidation of pyrite and chalcopyrite in this environment is geologically slow. Above the water table, however, there is abundant oxygen, carbon dioxide, and moisture which is an optimum environment for bacterial leaching of sulfides. Oxidation of pyrite or chalcopyrite yields ferrous ion that then is oxidized to ferric ion by *T. ferrooxidans*, beginning a propagation cycle that promotes mineral dissolution. Formation of the first enrichment blanket is relatively inefficient because of the slow kinetics of chalcopyrite dissolution possibly due to surface passivation phenomena. The formation and preservation of this early cycle profile will, therefore, be dependent on the relative rates of chemical weathering and erosion. However, once chalcopyrite has been converted to chalcocite, subsequent leaching and enrichment cycles are more efficient. Seasonal and climatic cycles promote the growth of bacteria during wet periods. During dry periods, the evaporative concentration of the biogenic sulfuric acid and ferric sulfate promotes mineral dissolution and the formation of soluble salts such as chalcanthite. These salts, then, constitute the mobile fraction of minerals that are ready to be leached and transported during the next hydrologic pulse. Reduced carbon from dead *T. ferrooxidans* is flushed along with the other soluble minerals down to the water table where SRB populations thrive in anaerobic conditions (microenvironments) at pHs >5.5. In that environment, SRB may contribute to enrichment by reducing sulfate to sulfide (H₂S) preferentially precipitating copper as covellite instead of iron as a mono-sulfide prior to diagenesis to chalcocite.
Supergene processes end or slow down predominantly as a result of hydrologic, climatic, and tectonic effects. Although supergene processes would terminate if the source were depleted in pyrite or copper minerals and equilibrium chemical conditions were reached; these static conditions are unlikely to persist for very long in geologic time. Under certain geologic and climatic conditions, tectonic and climatic forces can work separately or in conjunction to impose drying conditions on the supergene profile or by shifting the location of the redox boundary. For example, sulfide zones can be stranded above the water table as in many areas of the Morenci district, or left to desiccate in dry climatic conditions such as in northern Chile since the mid-Miocene. In these environments *T. ferrooxidans* will die and geochemical reactions will proceed slowly in the absence of significant moisture. Alternatively, dynamic tectonic environments coupled with cyclical climatic conditions would promote deep leaching and the formation of thick supergene blankets such as Morenci.

The end result of these processes was that copper was efficiently leached and mobilized in the vadose zone. Soluble copper was then available to enrich chalcopyrite and pyrite to form secondary copper sulfides below the water table, thus converting a sub-economic copper occurrence into world class ore body over the last 10 million years. At Morenci, these naturally occurring bacteria are used to help leach the copper out of the ore in hydrometallurgical operations, making it one of the most productive copper mines in the world.
Introduction

A total of 26 samples were collected from representative profiles across the district to document the range of ages of supergene processes captured in the geologic record in the Morenci district. Previously published K-Ar dates on alunite from the district of 9.9 and 7.8 Ma (Cook, 1994) indicate that supergene mineralization formed during the mid- to late Miocene. Geologic evidence, however, indicates that it was permissible for enrichment to have formed in the Oligocene prior to mid-Tertiary volcanism, and for leaching and oxidation to have continued into the Pliocene and Pleistocene. The samples were collected from the top of the supergene profile in leached capping at Coronado, Metcalf, American Mountain, and Western Copper, at the base of the oxide zone at Northwest Extension, and through the enriched blanket and into the top of the hypogene zone at Metcalf and Western Copper. One sample of exotic malachite was also collected from the Clifton Tuff above the old Train Station in Clifton. The sample locations are shown on Figure 62 and detailed sample descriptions are included in Appendix E.

Selected samples from the suite were dated using $^{40}$Ar/$^{39}$Ar and $^{14}$C methods. A total of 16 new $^{40}$Ar/$^{39}$Ar ages have been determined for a suite of samples of alunite, jarosite, illite, and cryptomelane. In addition, a $^{14}$C date from a sample of malachite from the Clifton Tuff was obtained. The analytical methods and results are summarized below and shown in Tables 28 through 32, and in Figures 63 through 68.
Materials and Methods

The work was conducted at a variety of cooperating laboratories. Mineral separates were handpicked from the vein material and submitted to the Department of Geosciences X-ray Diffraction Laboratory at the University of Arizona to confirm the mineralogy. Selected manganese oxides and alunite samples were subsequently sent to the CVRD Laboratory in Belo Horizonte, Brazil for more detailed XRD analyses (Vieira, pers. commun). Splits of the samples were sent to outside laboratories for sulfur isotope determination, and for major oxide and trace element geochemistry as discussed below. The alunite and jarosite samples were also studied using reflected and transmitted light microscopy at the University of Arizona. A suite of 24 samples of alunite, jarosite, and illite were selected for dating at the New Mexico Geochronological Research Laboratory (NMGRL) in Socorro (Peters, 1999c). Subsequently, two cryptomelane samples were selected for dating at the Berkeley Geochronology Center (BGC) in California (Vasconcelos, pers. commun.), and a malachite sample was selected for dating at the Stable Isotope Laboratory in the Department of Geosciences at the University of Arizona (Dettman, in prep.). The NMGRL (Peters, 1999c) and BGC (Vasconcelos, pers. commun.) reports are included in Appendix B.

Alunite, Jarosite, and Illite Samples

A total of 19 samples of alunite, 4 samples of jarosite, and one illite were ultimately selected for $^{40}$Ar/$^{39}$Ar dating (Figure 62, Table 28). These samples were further
examined at the New Mexico Bureau of Mines microprobe lab to determine their prospects for dating, because small amounts of sericite and kaolinite and variable amounts of quartz contaminate some the samples. The amount of quartz has no effect on the date; however, sericite is a potassium-bearing hypogene mineral and can yield anomalously old apparent ages. In addition, small amounts of contaminant clay can also greatly elevate the apparent age of alunite samples (Polyak et al., 1998). A total of 14 of these samples contained dateable alunite and 4 contained dateable jarosite. The alunites were analyzed by the incremental heating method using a double-vacuum resistance furnace or a CO2 laser (Peters, 1999c). Contaminants in four of the samples (#229, #245, #246, and #281) were significant enough to cause problems cleaning the gas and they were not analyzed (Peters, 1999c). One sample (#279a) contained a mixture of alunite and jarosite and was not selected for further study (see Geochemistry section below). Abbreviated methods for the samples from Peters (1999c) are included in Appendix B. Standard analytical procedures are described in Heizler et al. (1999).

Mn-oxide Samples

Two suites of manganese oxide samples were studied. The initial suite was collected from near-surface exposures in the Southside, American Mountain (Gold Gulch), and Northwest Extension areas. XRD analyses, however, found only non K-bearing manganese oxide minerals consisting of todorokite, birnessite, and pyrolusite (Table 11) (Vasconcelos, pers. commun.). Three samples of manganese-oxide mineralization were subsequently collected from the base of the oxide zone in the Las Terrazas fault at
Northwest Extension (Figure 62, Table 28). X-ray diffraction analyses (Vieira, pers. commun.) of this mineralization revealed that it contains a highly variable mixture of cryptomelane, hollandite, hausmannite, and todorokite (Table 11) in addition to a zinc-manganese-oxide mineral (Zn$_2$Mn$_3$O$_8$). Subsequent crushing and hand picking yielded a number of clean grains of cryptomelane - hollandite from two of the samples for dating. The samples were sent to the University of Queensland, Australia for irradiation and were analyzed using the $^{40}$Ar/$^{39}$Ar method at the BGC. Standard analytical procedures are described in Vasconcelos et al. (1994b).

Malachite Samples

Exotic malachite mineralization fills fractures and voids in the Clifton Tuff and Basaltic Andesite down gradient from the Morenci district in the lower Chase Creek area and in the surrounding hills near Clifton. The mineral was identified in the field based on its effervescence in dilute hydrochloric acid. Traditional interpretations of this mineralization have concluded that copper oxides were deposited as a result of local smelter operations in Clifton (Pawlowski, pers. commun.); and indeed, green (non-carbonate, conicalcic?) copper mineralization occurs on bricks and blocks in the old historic concentrator foundation in downtown Clifton. Because copper oxide mineralization in the Clifton area occurs in veins and as fracture filling in basaltic andesite and Clifton Tuff, much of this mineralization may be exotic rather than anthropogenic.

To evaluate this, samples of these materials were submitted to the Stable Isotope Laboratory in the Department of Geosciences at the University of Arizona for carbon and
oxygen stable isotope analysis. Samples of the malachite were removed from the matrix rock using a 0.5 mm diameter drill bit, dissolved in dehydrated phosphoric acid, and the evolved CO₂ was cryogenically separated from water and other gases (Dettman, pers. commun.). Stable isotope ratios (δ¹³C and δ¹⁸O) were measured on a Finnigan MAT stable isotope, gas source mass spectrometer. The data were normalized to VPDB using the NBS-19 calcite standard, and the precision was reported to be better than 0.1 per mil for both δ¹³C and δ¹⁸O (Dettman, pers. commun.). The ¹⁴C measurement was made using CO₂ gas from the sample at the University of Arizona Accelerator Mass Spectrometry facility (AMS). Details of the operation of the U of A facility and mathematics of the ¹⁴C calculations are given in Jull et al. (1986), Linick et al. (1986), and Donahue et al. (1990).

Sulfur Isotope Studies

Sulfur isotopes can be used as a method to distinguish hypogene alunites from supergene alunites (Field, 1966; Field and Gustafson, 1976, Ohmoto and Rye, 1979). Their work indicated that sulfate in hypogene alunite tends to be fractionated with respect to hypogene sulfide resulting in δ³⁴S values greater than +8 per mil. In addition, supergene sulfates, including alunite and jarosite inherit sulfur from hypogene sulfides without significant isotopic fractionation, and retain δ³⁴S values between –3 and +1 per mil in most porphyry systems. Therefore as an additional check on the field and petrographic work, the alunite and jarosite samples from the geochronology suite were submitted to outside laboratories for sulfur isotopic analysis in two phases of work. The first phase was an orientation study of four jarosite and two alunite samples that were submitted to R.E. Rye
for analysis at the U.S. Geological Survey Stable Isotope Laboratory in Denver. The second phase included the remaining alunites and jarosites, and samples of pyrite, chalcocite, and covellite from co-existing sulfides that were intermixed in four of the alunites. The second suite was sent to C.J. Eastoe for standard SO₂ sulfur isotope analysis in the Stable Isotope Laboratory in the Department of Geosciences at the University of Arizona following the methods of Robinson and Kusakabe (1975) and Coleman and Moore (1978). Copies of these reports are included in Appendix B.

Major and Trace Element Geochemistry

All 24 samples of alunite, jarosite, and illite were submitted to Activation Laboratories Ltd. (ACTLABS) in Ontario, Canada for geochemical analyses. The samples were handpicked grains from splits of the same samples that were submitted to the NMGRL for dating. Major element concentrations were measured using fusion ICP methods (ACTLAB code 4LITHORES-MAJ ELEM FUS ICP). Concentrations of a suite of 43 trace elements were measured using fusion ICP-MS methods (ACTLAB code 4LITHORES-TRACE ELEM FUS ICP/MS). The analyses were done using “Research Grade” protocol and the results were reported to their lowest detection limit.

**Geochemistry Results**

Sulfur Isotope Studies

The sulfur isotope results are consistent with a supergene origin for the alunite and jarosite at Morenci. With one exception, the δ³⁴S results for alunite, jarosite and their co-
existing sulfides ranged from –2.0 to +2.0 per mil with a mean of +0.6 per mil (Table 29). Overall, alunites in the Morenci district averaged +1.5 per mil and were slightly enriched in $^{34}\text{S}$ relative to jarosites (-0.2 per mil) and their co-existing sulfides (-1.3 per mil) as shown on the histogram in Figure 63. For comparison, Cook (1994) reported slightly more enriched values (3.5 and 5.8 per mil) from Metcalf and Morenci, respectively. The one exception was sample #245, which had anomalously light $\delta^{34}\text{S}$ values of –30.8 from chalcocite (Mazdab, pers. commun), and –20.5 and –15.8 per mil from samples of chalcocite coating pyrite (Eastoe, pers. commun.). Transmitted and reflected light microscopy of this sample revealed the presence of mineralized microfossil sulfate-reducing bacteria, and the isotopically light signature in sample #245 has been interpreted to be a result of biogenic fractionation (this study).

Alunite and Jarosite Geochemistry

Major and trace element geochemical data for the samples are shown in several tables and figures. Major oxide element geochemical results are included in Table 30. The calculated modal mineralogy of the samples was estimated from the major oxide geochemical data as shown in Table 31 and used to separate the samples into principal types as shown on Figure 64. Selected trace element data are shown in Table 32 according to principal type. The average trace element contents of the principal sample types are displayed on the log concentration plot in Figure 65a. The average rare earth elemental (REE) compositions of the sample types are plotted relative to upper continental crust abundance from Taylor and McLennan (1985) in Figure 65b.
Interpretation

The geochemical data support the distinction of three principal types of alunite and jarosite based on field relationships, XRD patterns, and reflected and transmitted light microscopy as shown in Figure 64 and summarized in Table 33. The three types include: Type I white alunite, Type II green alunite, and Type III brown to yellow jarosite, and show a progressive change in geochemistry with increasing degree of leaching. Although the general locations where these types of alunite and jarosite occur are noted below, they do not appear to be unique to a particular supergene zone.

Type I samples are typically white to cream or tan colored and found in the enriched blanket or in remnant sulfide volumes in partially leached zones typically associated with pyrite +/- chalcopyrite, chalcocite, and covellite. White alunites are most commonly associated with single generation alunite, although two generations were found in a few samples. Calculated modal mineralogy (Table 31) indicates that Type I samples are almost pure alunite with less than 2% as jarosite and highly variable amounts of quartz and kaolinite. Type I samples exhibit a distinctive trace element geochemical signature (Table 32) with low average copper and molybdenum contents (138 PPM Cu, 21 PPM Mo) and elevated average zinc and lead contents (189 PPM Zn, 678 PPM Pb). Type I samples also contain elevated levels of barium (1,417 PPM), strontium (1,305 PPM) and cerium (375 PPM). Copper and zinc are known to substitute for Al$^{3+}$ or Fe$^{3+}$, and lead, barium, strontium and cerium are all known to substitute for K$^+$ in alunite and jarosite (Scott, 1987; Alpers et al., 1989).
Type II samples are typically yellow to pistachio green or olive green and found in the leached zones usually associated with hematite. Green alunites occur as one or two generations, typically filling open spaces in leached veins and fractures. Calculated modal mineralogy (Table 31) indicates that Type II samples are mixtures or substitutions of about 95% alunite and 5% jarosite with much lower amounts of quartz and kaolinite compared to Type I samples. Type II samples also exhibit a distinctive trace element geochemical signature (Table 32) with high average copper and molybdenum contents (2,572 PPM Cu, 373 PPM Mo), only traces of zinc (35 PPM), and no lead (<5 PPM). Type II samples also contain elevated levels of barium (2,709 PPM), but much lower average levels of strontium (194 PPM) and cerium (31 PPM).

Type III samples are typically yellow to brown and found in the leached zones always associated with hematite, and with pyrite in places. Jarosite (hardness 2-1/2 to 3-1/2) is softer than alunite (hardness 3-1/2 to 4) and rarely survived sample preparation for thin and polished sections; therefore, data on multiple generations are available for only one sample (#279b) which exhibited two generations. Calculated modal mineralogy (Table 31) indicates that Type III samples are typically pure jarosite with highly variable amounts of quartz and kaolinite. One sample (#279a) was clearly a vein that contained alunite and two generations of jarosite, and was not selected for age dating. Type III samples exhibit an intermediate trace element geochemical signature compared to Type I and II samples (Table 32) with high average copper and molybdenum contents (1,236 PPM Cu, 193 PPM Mo), slightly elevated levels of zinc (35 PPM), and high levels of lead (1,458 PPM). Type III samples contained slightly lower levels of barium (905 PPM) and
strontium (139 PPM), intermediate levels of cerium (86 PPM) relative to the other sample
types.

Trace element patterns for the three types of samples display a progressive change
in geochemistry with increasing degree of leaching (Figure 65, Table 33). Type I samples
typically contain grains of pyrite +/- chalcocite, quartz, and wall rock, relatively low
levels of copper and molybdenum, and high levels of zinc and lead. These samples are
interpreted to have formed during or after the enrichment zone within which they occur. At
this point in space and time, supergene solutions would have been depleted in copper,
contain little molybdenum due to its low solubility, and relatively high levels of zinc and
lead because of their higher solubility. Type II samples, on the other hand, typically fill
quartz-hematite veins, exhibit multiple generations of alunite, and contain grains of
hematite in the alunite. These samples contain relatively high amounts of copper and
molybdenum and are depleted in lead and zinc. These samples are interpreted to have
formed during or after the leaching event that affected the supergene zone in which they
occur. At this point in space and time, supergene solutions would have been enriched in
copper and molybdenum, but contained little zinc and lead, having already been depleted
from the zone. In addition, kaolinite formation may have been limited by buffering of the
wall rocks of the veins and fractures by reaction with earlier solutions, thus accounting for
the low relative kaolinite contents of Type II samples. Type III samples contain more
variable levels of trace elements and are interpreted to have formed contemporaneous with
or later than the leached zone within which they occur. Their trace element geochemistry is
probably indicative of the remaining leachable mineralization in the local environment.
The REE plot (La through Lu) in Figure 65b contains hypogene illite for comparison. This diagram indicates a progressive depletion of the heavy rare earth elements with increasing degree of leaching and further supports the notion that Type I alunite is formed in a different geochemical environment than Type II alunite and Type III jarosite.

Based on the evidence discussed above, it is postulated that alunite and jarosite record different events, but all occur at a late stage in a particular supergene cycle (Table 33). Type I alunite appears to indicate the end of the formation of the enriched blanket within which it occurs. If leaching of overlying material is required before an underlying enriched blanket can be formed; then, Type II alunite appears to indicate the end of the formation of leached capping and the beginning of the formation of a later-cycle enriched blanket. Finally, Type III jarosite appears to indicate later destruction of remnant sulfides in the zone of leaching and oxidation under conditions with greater Fe$^{3+}$/Al$^{3+}$.

Carbon and Oxygen Isotopes

The sample of exotic malachite from the Clifton Tuff yielded a d13C result of –1.17 per mil (relative to PDB) and a δ18O result of +25.6 per mil (relative to SMOW) (Dettman, pers. commun.). These results are consistent with data for naturally occurring malachite at Northwest Extension (Melchiorre et al., 1999; Melchiorre, 1998).

Geochronology Results

The results from this study support the assumptions and hypotheses developed in the preceding chapters about the timing of supergene enrichment in the Morenci district.
None of the alunite samples yielded ages that date the Laramide hydrothermal event. With one exception (illite), all of the samples that were dated are considered to be of supergene origin.

**Alunite, Jarosite, and Illite Samples**

\(^{40}\text{Ar}/^{39}\text{Ar}\) ages for sulfates from the Morenci district ranged from 13.4 to 0.9 Ma with a mean and mode of 7.4 Ma. The NMGRL preferred ages for the alunite, jarosite and illite samples and their type are listed in Table 28 and shown on the histogram in Figure 66. Weighted mean ages were calculated for 12 of the samples with at least 50% of the \(^{39}\text{Ar}\) released and acceptable MSWD values (Peters, 1999c). Seven other samples yielded age spectra that climbed monotonically with increased heating; however, Peters (1999c) calculated weighted mean ages for the three samples with the least disturbed spectra. Two alunite samples yielded very low-resolution age spectra with over 99% of the \(^{39}\text{Ar}\) released in one step. The illite sample also yielded a disturbed age spectrum; however, Peters (1999c) calculated a total gas age for this sample. The detailed results are included in Appendix B.

**Mn-oxide Samples**

The preferred \(^{40}\text{Ar}/^{39}\text{Ar}\) age for a sample of cryptomelane - hollandite from the Northwest Extension area is 7.59 +/- 0.12 Ma (Vasconcelos, pers. commun.). This also compares well with the other ages of supergene mineralization reported in Table 28 and shown in Figure 66. Full results are included in Appendix B.
Malachite Sample

The AMS lab reported that there was about 2% modern carbon (0.0172 +/- 0.0011 fraction) in the malachite sample (analysis number AA 36449) and a $^{14}\text{C}$ age before the present of 32,640 +/- 500 years (Dettman, pers. commun.). Unfortunately, the sample of drilled powder was exposed to atmospheric contamination for a week or two before it was reacted. According to W. Beck at the AMS lab, contamination due to interaction of finely ground powder with atmospheric CO$_2$ is possible; therefore, this age must be considered to be a minimum age for the sample. Nonetheless, this result confirms that the exotic malachite in the Clifton Tuff and basaltic andesite in the Clifton area is not anthropogenic. The results are included in Appendix B.

Interpretation

The $^{40}\text{Ar}/^{39}\text{Ar}$ results from this study support the conclusion from the sulfur isotope analyses that the Morenci sulfate samples are of supergene origin. The results are consistent with two previously reported K-Ar ages from alunite of Cook (1994) that fall within the range of values from the new work (Table 28, Figure 66). In general, the results follow a consistent pattern according to structural domain across the district as illustrated in Figures 67 and 68 and discussed in the subsequent section. The $^{40}\text{Ar}/^{39}\text{Ar}$ results fall into four categories: samples with flat age spectra, samples with climbing age spectra, samples that degassed in one step, and one sample with suspect $^{39}\text{Ar}$ recoil effects.
Nine of the samples displayed flat age spectra (#105, #242a, #248A, #250, #267, #268, #269, #278c, and #280b) indicative of simple argon systematics and their interpretation is straightforward (Peters, 1999c). With the exception of sample #250 and #267, thin section examinations, XRD analyses, and microprobe studies indicated that only one phase of alunite or jarosite was present. Although sample #250, a Type II alunite, contained two phases, the older phase was sparsely distributed in the vein and did not appear to be selected in the mineral separate. The age of this sample was 4.32 +/-0.04 Ma and is the youngest of the alunites tested at Morenci and is significantly younger than the 7.19 +/- 0.27 Ma K-Ar age of Cook (1994) from the same location. A plausible interpretation is that Cook’s sample represents the older generation of alunite in this area. The jarosite in sample #267 contained ~5% of a K-rich, clay-size contaminant (probably illite). Peters (1999c) reported that the last ~10% of the age spectrum showed a rise in apparent age and a drop in the K/Ca ratio and radiogenic yield. She also raised the possibility that the alunite and illite are not thermally distinct which would also affect the earlier part of the age spectrum as well. In this case, the weighted mean age of 8.34 +/- 0.22 Ma would be a maximum age for the formation of alunite in this sample (Peters, 1999c). For comparison, the cryptomelane – hollandite in sample #288 yielded an age of 7.59 +/- 0.12 Ma. Both of these samples are from the base of the oxide zone at Northwest Extension and are only about 168 m (550 ft) apart, however sample #288 is 15 m deeper and in the Las Terrazas fault zone while sample #267 is in the younger granite porphyry (Figure 68).
Seven of the samples displayed climbing age spectra (#9-3, #9-4, #238, #243, #247, #279b, and #282) and their interpretation is less straightforward (Peters, 1999c). In addition to quartz, microprobe studies and XRD analyses indicated that K-feldspar was present in samples #9-3 and #9-4 and a trace of kaolinite was present in sample #282. In addition, thin section examination indicated that multiple generations of alunite and jarosite were present in samples #9-3, #243, #279b, and #282 (Table 28). These observations are consistent with reports of climbing age spectra attributed to hypogene mineral contamination or multiple generations of sulfates in Vasconcelos (1999). Peters (1999c) reported maximum apparent ages for samples #9-3, #9-4, and #279b but no ages for the other samples with climbing age spectra. Samples #9-3 and #9-4 are from the same outcrop located about 137 m (450 ft) above, but in the same supergene profile, as samples #242a and #239 at Western Copper (Figure 67). All of these samples have ages that agree within error limits. Although two phases of jarosite are present in sample #279b, the youngest phase was sparsely distributed and did not appear in the mineral separate (Appendix E). The location and large error associated with this sample (0.87 +/- 1.3 Ma) allows its age to correspond with the age of the jarosite in sample #268 (Figure 67).

Two samples degassed in one step (#239 and #244) and the confidence in these ages is not high (Peters, 1999c). Thin section examinations and microprobe analyses indicated that two phases of alunite are present in sample #239 and possibly in #244. Peters (1999c) concluded that the apparent ages for these samples is probably an intermediate age between the two generations. The bulk of the material in sample #239 appears to be the younger, second-generation alunite (Appendix E). As discussed above,
the age for sample #239 is consistent within error limits of nearby samples at Western Copper (Figure 67). Sample #244 is located in the center of the tilted enriched blanket in the footwall of the War Eagle fault and appears to be mostly composed of one phase of alunite (Appendix E). Its location in the supergene profile at Metcalf and similar age (7.01 +/- 0.16 Ma) is consistent with other high-quality samples in the district (Figures 67 and 68).

The disturbed age spectrum from sample #249c appears to have been affected by $^{39}$Ar recoil and possibly complicated with excess Ar (Peters, 1999c). The sample is composed of fine-grained illite and would be subject to potential recoil affects, thus the integrated age of 61.0 +/- 1.6 Ma has a low confidence (Peters, 1999c). Despite these qualifications, the results clearly indicate that the illite in sample #249c is of hypogene origin and is consistent with similar ages for the Laramide-age porphyries in the district.
SYNTHESIS, CONCLUSIONS, AND RECOMMENDATIONS

Geologic studies of the Morenci district over the last 100 years record the evolution in our understanding of the extent and timing of processes in the supergene environment. Although all of the geologists who have studied the district recognized that enrichment occurred in multiple stages, they developed conflicting interpretations of the timing. In the early studies, Lindgren (1905a) and Moolick and Durek (1966) concluded that enrichment occurred in multiple cycles, but that supergene enrichment formed prior to mid-Tertiary volcanic activity. Langton (1973) thought that, although the bulk of enrichment was pre-volcanic, there was some redistribution during volcanism and there was a later stage of minor Miocene and Pliocene enrichment. In a significant departure from the previous work, North and Preece (1993) also recognized two generations of enrichment, but emphasized the importance of the post-volcanic enrichment to the development of the thick and high-grade enrichment profiles in the district from 30 to 10 Ma. Cook (1994) was the first to use K-Ar dating of alunite in the district and establish that enrichment occurred during the late Miocene. He further asserted that there was no evidence of pre-Miocene enrichment and that there had been profound lateral migration of supergene solutions in the district. The results of this study are consistent with Cook’s conclusions and provide further clarification and insight into the distribution, character, timing, and processes of supergene mineralization in the Morenci district.
Morenci Enrichment Cycles

The rocks in the Morenci district record a complex, episodic history of supergene enrichment that began over 13 million years ago and continues today. $^{40}\text{Ar}/^{39}\text{Ar}$ ages from alunite, jarosite, and potassium-bearing manganese oxides in the district record three cycles of enrichment and leaching, and a fourth cycle of leaching and destruction of the present enrichment blanket (Figure 66). These occurred in the mid-Miocene, late Miocene, early Pliocene, and Pleistocene epochs entirely during the second and third Cenozoic erosional periods in the Clifton-Morenci area. Although leaching and enrichment appear to have been episodic and related to disequilibrium caused by tectonism, these processes appear to have been nearly continuous from the mid-Miocene to the early Pliocene.

The four supergene cycles are shown along with the five stages of landscape evolution in Figure 69. This is a summary diagram showing the geologic processes that drove the formation of the Morenci porphyry copper deposit from the Laramide to the present. These processes include Laramide intrusion, hydrothermal alteration and mineralization, extension, volcanism, sedimentation, erosion, and chemical weathering. The four supergene cycles are described below.

First Cycle (18 to 12 Ma)

The first cycle of leaching and enrichment began in the mid-Miocene when the overlying volcanic rocks were eroded from the deposit. This cycle was coincident with the deposition of the conglomerate of Midnight Canyon during initial subsidence of the Duncan basin between about 18 and 12 Ma. Sample #280b, from the top of Meade Peak at
Coronado, records an alunite date of 13.39 +/- 0.08 Ma for the formation of the enriched blanket in this part of the district (Figure 68). Subsequent erosion of this first-cycle enrichment profile contributed small volumes of mineralized clasts to the overlying fluviatile deposits of Buzzard Roost Canyon as the Duncan basin continued to subside.

Second cycle (12 to 7 Ma)

The second cycle of leaching and enrichment began in the late Miocene when Basin and Range tectonism further dissected the district and deepened the Duncan basin. This cycle appears to have been the longest in duration and the most widespread. Eleven alunite, one jarosite, and one manganese-oxide ages, from samples collected across the district (Figure 62), record a cycle that began about 11.0 Ma and continued through 7.0 Ma, with a prominent maximum at 7.4 Ma (Figure 66). The older samples from this cycle contain one generation of Type I alunite and represent simple enrichment histories. The preponderance of multiple generations of alunite in the younger samples and the mixture of both Type I and Type II alunites indicate a significant change in enrichment late in this cycle. It may well be more appropriate to include the older samples from the second cycle with the first cycle. Although there are no samples with ages between 11.0 and 13.4 Ma, it is possible that leaching and enrichment continued during this time. In fact, rocks of the fluviatile deposits of Buzzard Roost Canyon contain a relatively uninterrupted sequence and increasing volumes of mineralized clasts upward in the section.

The oldest dates for this cycle are from alunites at the top of the enrichment profile at Metcalf (Figure 67, Cross Section B-B’). A cluster of samples (#92-21, #278c, and
#248a) in this area range in age from 9.88 +/- 0.26 Ma (Cook, 1994) to 8.82 +/- 0.08 Ma and show a local decrease in age with depth. Sample #269 is composed of alunite from a remnant sulfide zone in leached capping in the hanging wall block of the War Eagle fault at Metcalf (Figure 67, Cross Section A-A’). This sample has an age of 11.0 +/-0.24 Ma and is the second oldest supergene date in the district. Presumably, this structural domain was significantly higher in elevation prior to late Miocene faulting.

The bulk of the thick high-grade enrichment blanket and the Chase Creek Graben appears to have been developed by 7.0 Ma. Alunite with ages from 7.78 Ma to 7.0 Ma were found in the Metcalf, Western Copper, Northwest Extension, and American Mountain areas (Figures 67 and 68). All of the dates from alunite in the Western Copper profile (Figure 67, Cross Section C-C’) agree within error and average 7.6 Ma. A similar date of 7.01 +/- 0.16 Ma was recorded in alunite (#244) from the center of the enriched blanket in the footwall block of the War Eagle fault in Metcalf (Figure 67, Cross Section B-B’). Sample #244 is approximately 258 m below sample #248a (8.82 +/- 0.08 Ma) in the Metcalf profile and further supports the classical notion of decreasing age of enrichment with depth in this simple enrichment profile that is outside of the Chase Creek graben.

Enrichment and in-situ oxidation in the Northwest Extension area also occurred during this cycle. Sample #92-05 records a K-Ar age from alunite of 7.19 +/-0.27 Ma (Cook, 1994). This sample occurs at the top of the enrichment profile at Hennesey Hill in between Northwest Extension and Coronado (Figure 68, Cross Section D-D’). Presumably, this represents the age of the enriched blanket in this area that was formed by second-cycle leaching of a pre-existing, first-cycle blanket. The jarosite in sample #267
and the cryptomelane-hollandite in sample #288 record the leaching and \textit{in-situ} oxidation of this former blanket between 8.34 and 7.59 Ma, respectively. The first-cycle blanket at Northwest Extension may be correlative to the 13.39 Ma blanket at the top of Coronado. This enrichment profile was subsequently offset and preserved along the Las Terrazas fault in the late Miocene, after formation of the second cycle blanket. This appears to be similar to the structural development and preservation of 11.0 Ma enrichment in the hanging wall of the War Eagle fault on the eastern side of the Chase Creek graben, as discussed above.

Third Cycle (6 to 4 Ma)

The third cycle of leaching and enrichment began at the end of the Miocene and extended into the early Pliocene toward the waning stages of Basin and Range extension in the region. Sample #250, from the top of Hennesey Hill between Northwest Extension and Coronado, records an alunite date of 4.32 +/- 0.04 Ma for the formation of some enrichment in this part of the district (Figure 68). Enrichment in this cycle was formed from leaching of earlier-cycle enriched blankets leaving hematitic and jarositic leached caps above the enriched blanket. Sample #105, from the leached capping in the hanging wall of the War Eagle fault, records a jarosite date of 5.64 +/- 0.12 Ma for the formation of the leached capping in this part of the district.

During the second and third cycles, erosion of the supergene zone at Morenci continued shedding detritus into the adjacent Duncan basin. Structural deformation in the Duncan basin and adjacent bedrock blocks waned by the time the upper sediments of the Buzzard Roost Canyon were deposited. Rocks with copper oxide mineralization and
leached capping from a variety of rocks, and hematitic gossan material from the skarns in the district comprise up to 20% of the clasts in the overlying alluvium of Smuggler Canyon that were deposited as the Duncan basin slowly filled.

Slickenlines record oblique strike-slip movement on several fault planes in the Morenci district. These are particularly evident in places along the Garfield and Chase Creek faults. Samples #281 and #282, from the leached capping at the top of American Mountain, contain deformed alunite with oblique slickenlines (Appendix E). Although sample #282 yielded a disturbed age spectra, an age of about 7 Ma is consistent with similar samples in the district (Table 28). It is permissible, then, that the third-cycle of leaching and enrichment may have been initiated by oblique-slip deformation associated with the late structural adjustments within the Transition Zone. This would be consistent with late Miocene clockwise rotation of the Colorado Plateau during this cycle (Chapin and Cather, 1994).

Fourth cycle (2 Ma to present)

The fourth cycle of leaching began in the Pleistocene as a result of base-level drop caused by down cutting of the Gila River, and is continuing today. Samples #268 and #279b, from the top of Metcalf, record jarosite dates of 1.69 +/- 0.08 and 0.87 +/- 1.3 Ma, respectively for the formation of partial leaching that has destroyed portions of the enriched blanket in this part of the district (Figure 68). Exotic copper mineralization in the Clifton Tuff and basaltic andesite in the Clifton area records a $^{14}$C date of 32,640 +/- 500 BP, which is a minimum age for the sample. It is possible that exotic copper
mineralization was deposited at least since then, and maybe earlier when Chase Creek and
the San Francisco River began their incision into the Morenci district and adjacent basin
fill. Leaching and oxidation of the present blanket is continuing today, and can be observed
in action as the deposit is exposed during mining operations.

Conclusions

The inescapable conclusion from this study is that supergene enrichment in the
Morenci district is geologically young and related to the structural evolution of the district
from the mid-Miocene to the present. Mid- to late Tertiary erosion, tectonism, and
associated volcanism and sedimentation played a profound role in the formation and
preservation of the Morenci porphyry copper deposit. Although it was permissible for
enrichment to have occurred prior to Oligocene volcanic activity, there is no evidence
preserved in the rocks to substantiate this interpretation. Although there were at least four
supergene cycles, most of the enrichment appears to have been formed during the late
Miocene from about 11 to 7 Ma and coincides with Basin and Range extension in the
region.

Tectonics and structure at all scales are key first order controls of supergene
processes. These controls range from the original stockwork fracture density at a small
scale that affects huge volumes of rock, to faults at a larger scale that displace
mineralization and control the relative position of the groundwater table in response to
episodic tectonism. Field observations and mathematical modeling based on mass balance
principles indicate that lateral migration and enrichment was an important process in the
Morenci district. Calculated eroded thicknesses suggest that copper may have been transported from the topographically higher and peripheral areas of the deposit and deposited in the enriched blanket in the central graben because of district groundwater flow in this structural setting. Stacked supergene profiles and the distribution of secondary mineralization indicate that the Chase Creek graben formed an efficient trap for laterally migrating solutions that added copper to an already well mineralized domain. In this structural environment, thick supergene sulfide blankets that reveal multiple cycles of zoned secondary copper minerals may have been formed from the bottom to the top; the opposite of conventional models.

Supergene processes have affected almost all of the known Morenci deposit to varying degrees, and this effect extends to great depths (>500 m, >1,640 ft) below the surface. Supergene enrichment occurs in a continuous blanket of varying grade over a 19-km$^2$ (7.5 mi$^2$) area. These processes affected regions of the deposit differently depending on their ore and gangue mineralogy. Mineral zoning, then, controls the distribution and style of supergene mineralization throughout the district. For example, Northwest Extension, Metcalf Garfield, and Coronado occur in the north-central portion of the district where py/cc ratios are <2 and contain significant copper oxide zones. Thick high-grade regions of the enriched blanket occur in the Metcalf, Western Copper, and Morenci areas where the primary hypogene copper grade was highest, the quartz-sericite-pyrite alteration was strongest, and the py/cpy and py/cc ratios were the greatest (>4:1).

Microbiological and geological studies in the Morenci district reveal that acidophilic iron oxidizing bacteria (Thiobacillus ferrooxidans) and dissimilatory sulfate
reducing bacteria (SRB) contribute to leaching and enrichment of copper in the supergene environment. Sampling of actively weathering zones in the pit showed populations of *Thiobacillus ferrooxidans* reaching populations >$10^7$ MPN/ml and populations of viable SRB with over$10^3$ MPN/ml at some sites. Micro-fossilized SRB, similar in morphology to those grown in-vitro, were found encapsulated in alunite 95 meters (310 ft) below the pre-mine surface and 35 meters (115 ft) above the enriched blanket at Metcalf. Oxidation of pyrite and chalcopyrite yield ferrous ion that is subsequently oxidized to ferric ion by *T. ferrooxidans*, beginning a propagation cycle that promotes mineral dissolution. During wet events soluble minerals and reduced carbon from dead *T. ferrooxidans* are flushed down to the water table where SRB populations thrive in anaerobic conditions at pHs >5.5. In that environment, SRB may contribute to enrichment by reducing sulfate to sulfide (H$_2$S) preferentially precipitating copper as covellite prior to diagenesis to chalcocite. $^{40}$Ar/$^{39}$Ar dating of alunite at Metcalf indicate the micro-fossilized SRB are of late Miocene age and were formed during the second supergene cycle suggesting that these processes have been going on at least since then.
Recommendations

Despite the work that has been completed in the Morenci district over the last 25 years, significant questions still remain. Mines make great natural laboratories. In a district like Morenci, it seems like there is no end to research opportunities, some with direct applications to operations and exploration, others of more academic interest. Those that yield insights for both groups are particularly compelling. Key opportunities for future work are briefly outlined below.

Additional study of the basic geology of the Morenci deposit is still needed. Questions about the timing and petrogenesis of the intrusive rocks and the attendant alteration and mineralization are still unresolved. Intrusive relationships in the pit and recent studies of the dacite porphyry and the Silver Creek area indicate that the intrusive history of the district may be more complicated than we thought. At a district scale, alteration zoning is still not well mapped. Mapping and core logging have identified a later potassic vein assemblage at Coronado and a quartz-molybdenum assemblage at Metcalf, Morenci, and Garfield that cross cut earlier quartz-sericite-pyrite veins. District-scale mapping has shown that the early magnetite + biotite veins are very widespread, and in places chlorite replaces biotite. A detailed alteration study supported by a remote sensing technique such as hyperspectral imagery at a district scale would be useful and an excellent way to further study the distribution and character of alteration. Traditional igneous petrology and geochemistry linked with geochronological studies and detailed mapping of the intrusive rocks are clearly needed.
There are plenty of opportunities to study the district in support of exploration efforts at Morenci or for other porphyry copper systems. Metal zoning and fracture densities patterns could be studied over the 90-km$^2$ (33-mi$^2$) district that would be helpful to establish gradients and characteristics of the Morenci system. Large areas of undisturbed leached capping are still intact at Garfield, Western Copper, and American Mountain. These areas offer excellent sites to study the geochemistry and surficial exploration signature of leached rocks. A limited geochemical data set from Coronado indicates that study of the geochemistry of supergene enrichment for elemental dispersion and concentration patterns would be helpful to both explorationists and environmental scientists. In particular, the presence of zinc in the enriched blanket at Morenci is not consistent with Schurmann series sulfide replacement theory and deserves a closer look.

As the deposit is mined, there are excellent exposures to study and sample the mineralogy of the oxide and sulfide zones. In addition, there have been a number of geophysical surveys conducted over portions of the Morenci district in the last several decades. These surveys should be re-compiled and augmented with new surveys if appropriate.

Finally, the recent work that has been conducted in the district provides additional opportunities for further research. Now that a stratigraphic framework for the mid-Tertiary and younger volcanic and sedimentary rocks has been established, more detailed petrological and geochronological studies are possible. Further study of the role of microorganisms in the supergene environment at Morenci may yield new insights into the processes that form leached capping and enriched blankets that are directly applicable to SX/EW leaching operations. In some ways, the current mining and processing operations
are making sedimentary copper deposits in the leach stockpiles, and then partially leaching them to recover some of the copper. As re-mining of the older stockpiles proceeds, there is an opportunity to study the sedimentology, hydrology, and geochemistry of leaching. Finally, alunite and jarosite contain four stable isotope sites, and complete analyses of δD, δ18O_{SO_4}, δ^{18}O_{OH}, and δ^{34}S can provide powerful information about their environment of formation and insights about the paleoclimate and landscape evolution during that time.

Geologic research at Morenci over the last 25 years has built on the work of many other geologists since Waldemar Lindgren first studied the district almost 100 year ago. As we enter the 21st century, we are fortunate to have a sound geologic foundation on which to build. The potential of continued basic geologic observations from mapping, drilling and other studies, combined with the use of our extensive computer databases, GIS format maps, GPS applications, modern analytical techniques, and the keen minds of trained geologists is exciting.
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