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PETROGRAPHIC, GEOCHEMICAL, X-RAY, AND STABLE ISOTOPE STUDIES AT THE MORENCI PORPHYRY COPPER DEPOSIT, GREENLEE COUNTY, ARIZONA

by

Brad Thomas Calkins

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DEPARTMENT OF GEOSCIENCES

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1997
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This thesis has been approved on the date shown below:

[Signature] [Date]

John M. Guilbert
Professor of Geology
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DEDICATION

To my wife Linda, whose confidence in my scholastic ability was not only the spark behind my returning to school but also the unwavering support I needed throughout this process.

Also to my parents Dellos and Donna Calkins, who impressed upon me the value of an education at a very early age.
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ABSTRACT

Morenci is located in southeast Arizona. Copper grade hypogene mineralization averages 0.15%; one or more generations of supergene enrichment have increased mineralization to 0.96%. Intense supergene alteration has made it difficult to determine phyllosilicate paragenesis. The purpose of this study is to differentiate hypogene from supergene phyllosilicates.

Forty-nine samples from 5 drill holes were obtained for petrographic, geochemical, mineralogical, and stable isotope data. Petrographic examination, X-ray diffraction, and X-ray powder camera techniques established alteration of feldspars to kaolinite, montmorillonite, and sericite. Whole rock analyses using XRF determined cationic gains and losses that correspond with kaolinite and sericite. Stable isotopes of oxygen and hydrogen using kaolinite and sericite from 14 samples were tested to determine provenance of water. Stable isotope data show a trimodal distribution of phyllosilicates consistent with early hypogene alteration of magmatic origin, and two generations of supergene enrichment due to meteoric waters.
CHAPTER 1
INTRODUCTION

Statement of Problem

Copper mineralization at Morenci is the end result of some combination of magmatic-hydrothermal and chemical weathering processes. The effect of interaction of supergene alteration superimposed upon hypogene-altered rocks poses the major problem of this study; it generally complicates the interpretation of porphyry copper deposit geology. The study of silicate alteration assemblages has been used by many workers to formulate theories as to how porphyry copper deposits form (Schwartz, 1947, 1956; Sheppard, Nielsen, and Taylor, 1969, 1971; Lowell and Guilbert, 1970; Guilbert and Lowell, 1974; Hollister, 1978; Beane and Titley, 1981; Beane, 1982). The study of hydrothermal alteration at Morenci is difficult because of mesoscopic textural destruction due to pervasive argillic and phyllic alteration. The purpose of this study is to combine petrographic, geochemical, and isotope studies to differentiate among alteration minerals formed by hypogene and supergene processes.

The origins of alteration minerals associated with copper sulfides are important to discern. The formation of hypogene minerals is a consequence of original hydrothermal mineralizing processes, and their nature and distribution is governed by structural, chemical, temporal, lithologic, and tectonic factors of the hypogene environment. The distribution of supergene minerals is related to surface topography, climate, local pyrite content, fracture permeability, host rock lithology, and groundwater distribution at the
Figure 1.1 Index map of Arizona showing the location of Morenci
time of secondary enrichment, and their distribution will be limited to certain parts of the hypogene ore body (Cameron, 1961).

Location

The Morenci porphyry copper deposit is in Greenlee County in southeast Arizona (Figure 1.1) at an average elevation of 1463 meters (Moolick and Durek, 1966). Morenci is 170 air-line km NE of Tucson, and is most easily reached by Interstate 10 from Tucson to Willcox, then by U. S. Highway 191, formerly 666, through Safford and Clifton. Morenci lies on the boundary between the Basin and Range physiographic province to the south and the Transition Zone to the north (Preece, 1993). The ore deposit is in Sections 4, 8, 9, 15, 16, and 17, Township 4S, Range 29E on the Clifton 7.5 minute quadrangle (Figure 1.2)

Terminology

In this thesis, "hydrothermal solution" is a hot aqueous solution of unspecified origin. "Magmatic water" is water that has equilibrated with a magma at late magmatic temperatures, without regard to its source or origin. "Meteoric water" is water that has passed through and equilibrated with the atmosphere as precipitation and is present as surface water or groundwater (Sheppard, Nielsen, and Taylor, 1969; Guilbert and Park, 1986). "Hypogene" refers to ore and alteration due to ascending hydrothermal solutions (Sheppard, Nielsen, and Taylor, 1969); "supergene" refers to ore and alteration due to descending oxidizing solutions generally of acidic pH
Figure 1.2 Clifton quadrangle 7.5 minute topographic map provisional edition 1989, United States Geological Survey.
(Guilbert and Park, 1986). "Sericite" refers to a fine-grained white or green dioctahedral mica.

**Definition of Zones**

There are 3 distinct mineralogical-chemical vertical zones in most porphyry copper deposits (Figure 1.3): a zone of oxide-leach, an enrichment zone, and protore (Ransome, 1913; Emmons, 1917; Bateman, 1950; Guilbert and Park, 1986). The zone of oxide-leach, or leached capping, is above the zones of enrichment and protore and is characterized by altered rock that has undergone copper leaching by sulfuric acid ($\text{H}_2\text{SO}_4$) and ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) generated by the oxidation of pyrite by meteoric waters.

![Diagrammatic representation of oxidation and supergene enrichment of a porphyry copper deposit.](image)

Figure 1.3 Diagrammatic representation of oxidation and supergene enrichment of a porphyry copper deposit (adapted from Saegart, Bell, and Kilpatrick, 1974). A and B are irregular upper and lower boundaries of the zone of enrichment and are positioned as a function of permeability, sulfide content and distribution, and faulting.
The location and extent of the enrichment zone is dependent upon rock permeability, pyrite and chalcopyrite content and distribution, and oxidation potential of the chemical environment as a function of the availability of free oxygen. The highest natural oxidation potential is that of the atmosphere. Oxidation potentials approaching atmospheric values are present in air-filled pores in the zone of aeration above the water table (Anderson, 1982). The water table represents a boundary between oxidation above and reduction below for copper and iron minerals. Sulfide minerals are stable in reducing environments but release metal and sulfate ions in oxidizing environments. Metal ions are carried downward by periodic flushing by meteoric water, recharging the groundwater table, where they can be precipitated due to low-oxidation potential below the water table. Secondary enrichment at Morenci is characterized by chalcocite plus or minus covellite that has coated and replaced chalcopyrite and pyrite, beginning at the rims of mineral grains and along fractures, gradually pervading the entire mineral.

Protore mineralization at Morenci consists of disseminations, fracture fillings, and veinlets of chalcopyrite, pyrite, bornite, and molybdenite, with trace amounts of silver and gold. Protore as originally defined by Ransome (1913, p. 721) is rock that is "valueless material which generally underlies ores formed by sulphide enrichment and which would itself be converted into ore were the enriching process continued to sufficient depth." This definition holds true for most hypogene mineralization at Morenci where its tenor is too lean to mine, but not at other porphyry copper deposits such as San Manuel where hypogene sulfides are of sufficient grade to be mined at a profit (Titley, 1982b; Guilbert and Park, 1986).
Methods of Investigation

Five diamond drill holes were chosen from the Morenci district from which a vertical profile from oxide-leach zones at the surface to protore at depth could be obtained. These holes were chosen from various parts of the deposit (Figure 1.4) and are located in different structural blocks that may have experienced supergene processes at different times (Preece, 1993). Identification of the different vertical zones was accomplished by examining drill hole logs for elevation, lithology, alteration, and mineralization. The range of elevation from which all samples were taken is from 1821 meters to 899 meters. A total of 49 samples were selected, 10 samples each from drill holes A-491, WC-31, 1130, and 1132, and 9 samples from drill hole 1193. The 49 samples selected represent physical and chemical conditions in the oxide-leach, enriched, and protore zones across the deposit.

Silicate alteration is quantified and described by mineralogical, textural, geochemical, and isotopic data. Petrographic examination of polished thin-sections, X-ray diffraction analysis (XRD), and X-ray powder camera techniques were used to establish alteration mineralogies. Whole rock major and trace element geochemical analyses using X-ray fluorescence (XRF) were performed to obtain data on cationic gains and losses versus depth. Stable isotopes of hydrogen and oxygen from kaolinite and sericite were determined to ascertain provenance of waters involved with silicate alteration and mineralization.
Figure 1.4 Geologic Map of Morenci (Adapted from Phelps Dodge Morenci, Inc. Geology Department, 1993) also showing the locations of the 5 drill holes studied in this report and the profiles A-B-C and D-E of Figures 2.1 and 2.2.
Mining History

In 1863, scouts of the California Volunteers pursuing Apaches were the first non-natives to notice mineralization in the district (Watt, 1956). The first mining was for placer gold in 1870 on the Arizona Central Mine claim. Mining of copper at Morenci began in 1872 with extraction of high-grade oxidized replacement deposits of azurite, malachite, brochantite, chrysocolla, and cuprite in Paleozoic limestone and shale (Raymond, 1874; Wendt, 1887; Lindgren, 1905b; Reber, 1916; Butler and Wilson, 1938). In May 1886 the Detroit Copper Company began to operate the first copper concentrating plant in Arizona (Colquhoun, 1970). By 1903, “copper oxide” ore was exhausted and mining was begun on fissure veins in which secondary supergene chalcocite was the important ore mineral (Lindgren, 1905b). As higher grade ore was depleted, and technology progressed to allow lower grades of material to be mined, more of the wall rock was taken as a disseminated supergene enriched porphyry deposit by open-pit mining (Butler and Wilson, 1938). Leaching of low-grade copper oxide material with sulfuric acid from the Humbolt tunnel was first successfully accomplished at Clifton by the Arizona Copper Company in November 1893 (Colquhoun, 1970). In 1896 The Arizona Copper Company was also the first to concentrate low-grade sulfide material from rock which up to that time was considered waste (Colquhoun, 1970). Stripping was begun in 1937 at Morenci, in 1970 at Metcalf, and in 1989 at Northwest Extension (Freece, 1993).
Previous Work

First mention of the Clifton district with regard to its mining potential was by Raymond (1874). Wendt (1887) published the first geological work on the Clifton district. The first major publication of modern geologic writing was by Lindgren (1905b), who combined petrographic and geochemical methods with a field mapping project. Tolman (1909) wrote on methods used to extract chalcocite from the altered porphyries. Geologic information that had become available since 1905 was updated by Reber (1916), along with whole rock chemical gains and losses in monzonite porphyry calculated using Lindgren's (1905b) data. A brief history of ore production was given by Butler and Wilson (1938). Paragenesis of alteration was described by Schwartz (1947) from petrographic microscopy. Watt (1956) wrote on the discovery of mineralization and subsequent development of the district. MooHlick and Durek (1966) gave a history of mining operations and tell of copper oxides being in contact with over-lying basalts along with a different interpretation on the paragenesis of alteration than Schwartz (1947). Livingston, Mauger, and Damon (1968) state that erosion, leaching, and enrichment had occurred prior to deposition of Mid-Tertiary volcanics, and suggest the Mid-Tertiary rocks have protected the deposit from complete destruction. An interesting account of the early days of mining in the Clifton-Morenci district, and of James Colquhoun the general manager of the Arizona Copper Company is given by James Clifton Colquhoun (1970), his son. Interpretation of alteration zoning and structural history of the district that were believed to influence the emplacement of the intrusives was written by Langton (1973).
Bennett (1975) wrote on characteristics, mineralization, and origin of breccia bodies at both Morenci and Metcalf.

**District Geology**

**Pre-Laramide Rocks**

Basement lithology is Precambrian granite in the northern portion of the district and Precambrian granodiorite in the south (Figure 1.4). There are 305 meters (Lindgren, 1905b) of internally conformable Paleozoic sedimentary rocks consisting of a basal Cambrian Coronado quartzite, Ordovician Longfellow limestone, Devonian Morenci shales, and lower Carboniferous Modoc limestone, which lie nonconformably on the Precambrian rocks (Langton, 1973). No Triassic or Jurassic rocks are present (Lindgren, 1905b). The Cretaceous Pinkard formation lies disconformably upon the Modoc limestone (Lindgren, 1905b; Langton, 1973).

**Laramide Intrusive Rocks**

Three stages of igneous intrusions (Figure 1.4) were emplaced during the Laramide Orogeny (75-50 Ma) beginning at approximately 65–63 Ma (Preece, 1986) with diorite porphyry that predates mineralization and alteration. Monzonite porphyry, dated at 56.6 +/- 1.7 Ma (Reynolds and others, 1985), is the most widespread and oldest Laramide intrusive to host mineralization. Diabase dikes intruded along east-west faults. The diabase has not been dated, but field relationships show it cuts monzonite porphyry and is cut by the granite porphyry complex (Langton, 1973; Griffin, Ring, and Lowery, 1993). Two generations of granite porphyry are present, an older
granite porphyry dated at 57.4 +/- 2.1 Ma (Bennett, 1975; Reynolds and others, 1985) that intrudes the monzonite porphyry and a younger granite porphyry that intrudes the older granite porphyry. Older granite porphyry hosts mineralization; the younger granite porphyry post-dates hypogene mineralization (Bennett, 1975). The early diorite porphyry is predominantly located in the southwestern portion of the district, granite porphyries dominate in the northeast, and monzonite porphyry falls between the two (Figure 1.4). Moolick and Durek (1966) state that weathering of the protore occurred prior to Mid-Tertiary volcanism with copper oxides being in contact with overlying basalt flows.

Post-Laramide Rocks

The district was subjected to volcanic activity from the Eocene to the Miocene and again in the Pliocene, during which the deposit was covered with volcanic rocks (Livingston, Mauger, and Damon, 1968; Langton, 1973). Emergent tectonic activity resulted in mass wasting and stream erosion with subsequent deposition of the coarse, poorly sorted Pliocene Gila conglomerate (Livingston, Mauger, and Damon, 1968) in the southeastern part of the district (Lindgren, 1905b).

Structural Characteristics

Structural evidence indicates that the Morenci District was stable throughout the Paleozoic and Mesozoic. The first marked disruption of the strata occurs at the time of the intrusive porphyries. Lindgren (1905b), Butler and Wilson (1938), Moolick and Durek (1966), and Langton (1973) all
mention a dominant NE strike of intrusions, veins, and dikes in the district (Figure 1.4). The Laramide orogeny in southeast Arizona is thought to have been caused by ENE-directed subduction of the Farallon plate beneath the North American plate at 75-50 Ma (Rehrig and Heidrick, 1972). High rates of convergence aided in structural preparation by causing epicontinental extension and allowing emplacement of plutons at high crustal levels (Titley, 1982b). Magmas have been preferentially emplaced into domes along paths of least resistance oriented ENE to E throughout the district (Rehrig and Heidrick, 1972).

There is evidence of burial by Oligocene volcanics (Livingston, Mauger, and Damon, 1968; Moolick and Durek, 1966); the tuff at Clifton located four miles away is dated at 33 Ma (Livingston, Mauger, and Damon, 1966). Spencer and Reynolds (1989) state that Mid-Tertiary volcanism was time-transgressive from east to west across southern Arizona.

The region was characterized by Lindgren (1905b p. 88) as a "broken-down edge of a plateau." He noted that normal faulting that he placed as occurring between the intrusion of the porphyries and the extrusion of the lavas along a northwest strike had broken the sediments into monoclinal blocks of varying size and shape. This structural event is late-Cenozoic, 13 Ma (Spencer and Reynolds, 1989) extension with resultant W-to NW-striking Basin and Range type normal faults that cut and offset the earlier northeast-trending Laramide structures.
Hydrothermal Alteration and Mineralization

Extensive textural destruction that resulted from pervasive hypogene phyllic and supergene argillic alteration has made study of hydrothermal alteration a difficult and time-consuming process. The alteration has changed the older granite and monzonite porphyries from rocks composed mostly of plagioclase with quartz and biotite phenocrysts together in a fine-grained matrix of quartz, orthoclase, and plagioclase into a finely matted aggregate of quartz and argillic minerals punctuated with pyrite and chalcopyrite.

Crosscutting relationships indicate the earliest veins are quartz-K-feldspar cut by quartz-molybdenite veins. Main-stage mineralization crosscuts both quartz-K-feldspar and quartz-molybdenite veins and consists of multiple generations of quartz-sericite-pyrite-chalcopyrite plus or minus bornite veins. These veins are associated with intense wallrock alteration. Preece, Stegen, and Weiskopf (1993) report two distinctive quartz-sulfide-sericite veinings: pyrite-rich and chalcopyrite-rich. A study was done to determine the age of the sericite at Morenci using the potassium argon method of dating, and a range of ages from 50.9 Ma to 52.6 Ma was obtained (Forrester, 1997). Hypogene protore in the district averages 0.10 to 0.15% Cu (Preece, Stegen, and Weiskopf, 1993) and is accompanied by phyllic alteration that overprints early potassic alteration.

Preece (1986) reported that fluid inclusion studies indicate that low to moderate salinity fluids (2-15 wt % NaCl equivalent) were associated with sulfide deposition. Hypersaline (30-45 wt % NaCl equivalent) brines were
found in the early potassic veins. Homogenization temperatures generally
decreased with paragenesis: 330-450° C in potassic veins, 310-360° C in
quartz-molybdenite veins, 340-370° C in quartz-sericite-chalcopyrite veins,
and 290-330° C in pyrite veins.
CHAPTER 2

PETROGRAPHY OF DRILL HOLE SAMPLES

Objectives and Techniques

The objectives of the analytical portion of this study were 1) to gather sufficient data to provide a basis for choosing samples used for X-ray diffraction and powder camera work, whole rock geochemical, and stable isotope analysis; and 2) to gather data on mineralogic and lithologic changes with depth. Petrographic analysis was performed on 49 samples from 5 drill holes (Figure 1.4) using 5.0-cm-diameter whole drill core. A polished thin section was made from each sample for petrographic determination of textural and temporal relationships among minerals and to evaluate alteration. Microscopic examination was augmented by placing each thin section in an empty 35 mm slide holder between two optically crossed Polaroid™ plastic films. These sandwiches were loaded into a color laser xerographic 35 mm slide holder for enlargement to 8 x 10 inches, or 8.1X (Guilbert and Yadao, 1997) permitting study of 95 percent of the thin section at one time. Color prints were made of all 49 sections with and without crossed polars.

Figures 2.1 and 2.2 detail the rock types in each individual drill hole based upon examination of drill core and the drill hole logs.
Figure 2.1 Fence diagram of lithology in drill holes 1132, 1130 at Northwest Extension, and 1193 in the Morenci pit. See Figure 1.4 for location of line A-C.

- DH 1132
- DH 1130
- DH 1193

Horizontal scale: 1 cm = 177 meters

Explanation:
- KT$_{OGp}$
- KT$_{Mp}$
- PC$_{Granite}$

Sample location

Bend in diagram
Figure 2.2 Fence diagram of lithologies in drill holes A-491 at Metcalf, and WC-31 at Western Copper. See Figure 1.4 for location of line D-E.
Sample Selection

From these 49 samples, 15 were chosen for stable isotope study based on petrographic analysis and examination of the respective drill logs. One sample was selected from the oxide-leach, enrichment, and protore zones of each drill hole; each is described below. Samples were chosen as the best representation based upon paragenesis and type of feldspar alteration; an attempt was made to select samples that exhibited both phyllic and argillic alteration in each zone. Samples are designated by their elevation in meters in each drill hole.

Results of Thin Section Analysis

Throughout the following discussion all percentages are volume percentage.
Drill Hole 1132

Oxide-Leach zone, Sample DH 1132: 1526-1529

The sample is Precambrian granite with anhedral 2-4-mm quartz (43%), anhedral 1.5-2.5-mm K-feldspar (44%), and a trace amount of euhedral 0.2-mm zircon. There are multiple generations of quartz microfractures, some of which contain trace euhedral pyrite and chalcopyrite. No sericite alteration haloes are seen surrounding the quartz microfractures. Hypogene alteration is shown as 0.5-1.0-mm sericite (12%) replacing plagioclase and along microfractures in K-feldspar grains, and rutile (0.5%) is present in the biotite. Quartz grains have microfractures and some quartz grains have begun to be altered to sericite along the fractures. Kaolinite (1%) replaces sericite present within the feldspars, and sulfide grains have been altered to hematite that imparts a reddish color to the kaolinite. There are multiple quartz and kaolinite veins that crosscut other quartz veins.

In Figure 2.3, vein #1 is filled with quartz and kaolinite.
Qtz looks secondary

Veinlets

Figure 2.3 DH 1132: 1526-1529
Enrichment zone, Sample DH 1132: 1258-1260

This sample is Older Granite Porphyry with subhedral 0.4-2.0-mm quartz phenocrysts (3.5%) and subhedral 0.4-mm K-feldspar (13%) phenocrysts in a matrix composed of minute quartz (40.5%) and sericite (11%). Hypogene mineralization has anhedral 0.5-mm pyrite (0.5%), anhedral 0.5-mm chalcopyrite (1.5%), and quartz-molybdenite veins with molybdenite deposited along both vein walls. Hypogene alteration is expressed by 0.05-1.0-mm sericite (20%) replacing plagioclase with relict albite twinning, leucoxene (2%), and rutile (1%) in biotite. Supergene enrichment has chalcocite (0.15%) and covellite (0.2%) coating chalcopyrite. Covellite replaces chalcopyrite in biotite phenocrysts. Alteration is exhibited by kaolinite (7%) present in K-feldspar, 1.0-5.0-mm sericite (<1%) replacing biotite, and pyrite altered to iron oxide.

In Figure 2.4, a centerline is present for only part of the length of vein #1; it is filled with mostly quartz, and some kaolinite. Vein #2 is filled with clay. A centerline is present in vein #3 that appears to be filled with kaolinite for part of its length, then sericite fills the vein which later gives way to quartz. No centerline is observed in vein #6. It is filled with mostly quartz and some kaolinite.
Protore zone, Sample DH 1132: 1159

Sample 1159 is Older Granite Porphyry with subhedral 1-3-mm quartz phenocrysts (4%), euhedral 0.4-0.8-mm biotite phenocrysts altered to muscovite (3.5%) in a matrix of 0.1-mm quartz (40%), and 0.1-mm sericite (19%) and 0.1-mm anhedral quartz (5%) in veinlets. Hypogene mineralization has anhedral to euhedral 0.05-mm pyrite (1.5%), and anhedral 0.02-mm chalcopyrite (1.5%) present. Most of the sulfides are located in the groundmass of the granite porphyry, although many of the chalcopyrite grains are found in biotite phenocrysts. Hypogene alteration is shown by 0.05-0.1-mm sericite (25.5%) replacing subhedral plagioclase, and some sericite is seen within quartz phenocrysts. Supergene enrichment shows covellite replacing chalcopyrite.
Drill Hole 1130

Oxide-Leach zone, Sample DH 1130: 1470

The sample is Older Granite Porphyry with 2-mm anhedral quartz phenocrysts (8%), 0.7-mm anhedral K-feldspar phenocrysts (5%), kaolinite that replaces K-feldspar (7.5%), 0.8-mm subhedral plagioclase phenocrysts that are totally replaced by sericite (18%) although they retain their original shape, and 0.6-mm anhedral unaltered biotite phenocrysts (1.5%). The matrix is composed of 0.04-mm anhedral quartz (24%), 0.06-mm anhedral K-feldspar (15%), 0.06-mm anhedral sericite (7%), kaolinite (4.5%), and veins of 1-mm anhedral quartz (9.5%). Fine, 0.3-mm chrysocolla (1%) is in veins. No sulfides are seen. Hypogene alteration shows plagioclase altered to sericite. Supergene chrysocolla is in veinlets, and kaolinite-quartz veins cross cut quartz veins that contain iron oxide particles. Secondary alteration shows K-feldspar altered to kaolinite, and pyrite altered to iron oxides.
Enrichment zone, Sample DH 1130: 1200

Sample 1200 is Older Granite Porphyry with 2-mm anhedral quartz phenocrysts (2.5%), 3-mm subhedral K-feldspar phenocrysts (8%), 1-2-mm subhedral plagioclase phenocrysts altered to sericite (10.5%), and 1-mm anhedral bleached biotite phenocrysts (0.5%). The matrix consists of 0.15-mm anhedral quartz (28%), 0.1-mm anhedral K-feldspar (5%), 0.08-mm anhedral sericite (17%), 0.05-0.1-mm anhedral quartz (26%) in veinlets, and a trace of kaolinite. Subhedral 0.8-mm pyrite (1.5%), and 0.5-mm anhedral chalcopyrite (0.2%) are disseminated throughout the porphyry. Chalcocite (1.2%) replaces both pyrite and chalcopyrite. There is some replacement of chalcopyrite by covellite in vein #3. Hypogene enrichment shows quartz-pyrite veins along with deposition of chalcopyrite and an association of biotite with sulfides. Hypogene alteration shows plagioclase altered to sericite, and leucoxene was noticed present with the bleached biotites phenocrysts. Supergene enrichment shows chalcopyrite enriched with chalcocite to a greater degree than is pyrite.

In Figure 2.7, a centerline is present in vein #1. The vein is comprised of quartz and K-feldspar. A trace of sericite is present. The grain size within the vein is coarse; the shape is anhedral. Vein #2 has quartz, kaolinite and sericite. Vein #3 is a quartz vein. Both pyrite and chalcopyrite are replaced by mostly chalcocite and some covellite.
Figure 2.7 DH 1130: 1200
Protore zone, Sample DH 1130: 1097

The sample is Older Granite Porphyry with 4-5-mm anhedral quartz phenocrysts (8.5%), 1-mm subhedral K-feldspar phenocrysts (8%), 0.5-1-mm subhedral plagioclase phenocrysts (28%) that are altered to sericite, 1-mm subhedral biotite phenocrysts (1.5%), and 0.06-mm aggregates of rutile (2%). The matrix consists of 0.03-mm anhedral quartz (16%), 0.3-mm anhedral K-feldspar (10.5%), 0.03-mm anhedral sericite (16.5%), kaolinite (0.5%) along with veins of 0.5-mm anhedral quartz (2%), and 0.8-mm K-feldspar (3%). Anhedral 0.4-mm pyrite (3%), 0.08-mm anhedral chalcopyrite (0.8%) are disseminated throughout the porphyry with chalcocite (0.2%) and covellite (0.5%) replacing chalcopyrite. Hypogene mineralization shows quartz-pyrite-chalcopyrite veins. Hypogene alteration displays plagioclase altered to sericite, although faint relict albite twinning is discernible, and biotite altered to rutile. Supergene enrichment shows chalcocite coating both chalcopyrite and pyrite, although covellite replaces chalcopyrite only. Subhedral bleached biotite is associated with sulfides, some of the biotite is altered to sericite. There are void spaces where biotite grains used to be present.

In Figure 2.8, vein #2 is filled mostly with quartz although feldspar clasts are also present. They appear to have been ripped away from the wall when the vein opened. No centerline is seen.
Figure 2.8 DH 1130: 1097
Drill Hole 1193

Oxide-Leach zone. Sample DH 1193: 1339-1342

This sample is Monzonite Porphyry with 0.3-mm quartz phenocrysts (0.5%), 0.25-mm quartz in veins (6.5%), 0.03-mm sericite replacing former plagioclase phenocrysts (24.5%), and 2-mm biotite phenocrysts (2%), together in a matrix composed of 0.02-mm quartz (24%), 0.02-mm sericite (24%), 0.3-mm K-feldspar (5.5%), and kaolinite (6%) replacing K-feldspar. Anhedral pyrite 0.5-mm (3.5%) and a trace of chalcopyrite are being replaced by chalcocite (2.5%) and covellite (0.5%). Hypogene mineralization exhibits quartz-pyrite-chalcopyrite veins with sericite alteration haloes. Many of the pyrite grains contain multiple fractures, as though they have been shattered. Hypogene alteration shows all plagioclase phenocrysts completely altered to fine-grained sericite with the original shape of the plagioclase phenocrysts preserved. Supergene enrichment displays chalcocite and covellite replacing chalcopyrite only. Coarse anhedral bleached biotites are associated with the sulfides, and sericite is altered to kaolinite. Kaolinite and cryptocrystalline quartz veins cut sericite.

In Figure 2.9, vein #1 appears to be cut by all other veins. No centerline is present. Vein #2 is filled with kaolinite as is vein #3 which is repeatedly offset. Vein #4 is filled with quartz-sericite-kaolinite. Chalcocite replaces chalcopyrite. Vein #5 is filled with fine-grained sericite, quartz, and chalcopyrite. Chalcocite replaces chalcopyrite; some covellite replaces chalcopyrite. Vein #7 is a kaolinite-quartz vein that cuts a quartz sericite vein.
Enrichment zone, Sample DH 1193: 1102-1103

Sample 1102-1103 is Quartz Monzonite Porphyry with 2-mm former K-feldspar phenocrysts altered to kaolinite (31.5%), 1-mm biotite phenocrysts (5%), and 1-mm plagioclase phenocrysts altered to sericite (5%). The matrix consists of 0.05-mm quartz (24%), kaolinite (18.5%), 0.02-mm sericite (8%), 0.2-mm biotite (5%), 0.1-mm K-feldspar (1%), and 0.04-mm aggregates of rutile (0.8%). Anhedral 0.7-mm pyrite (0.6%) and a trace of chalcopyrite are located in veinlets. Hypogene mineralization shows quartz-pyrite-chalcopyrite veins that cut feldspar grains. Hypogene alteration altered plagioclase to sericite and biotite to rutile and sericite. Supergene enrichment displays chalcocite and covellite replaced chalcopyrite only. Feldspars both as phenocrysts and in the matrix are almost completely argillized. The sulfides are surrounded with iron oxide haloes.

In Figure 2.10, K-feldspar is located within vein #1 along with chalcopyrite. Vein #2 has quartz along with sericite and pyrite. A brownish stain is given off by the pyrite.
Figure 2.10 DH 1193: 1102-1103
Protore zone, Sample DH 1193: 899-900

Sample 899-900 is Precambrian Granite with 2-mm subhedral quartz (17%), fine pulverized 0.05-mm quartz (18%), 2-4-mm anhedral K-feldspar (20%), 1-2-mm subhedral plagioclase (9%), and 0.2-mm subhedral zircon (0.5%). Alteration is characterized by 0.03-mm sericite (16%) in plagioclase, kaolinite (14%) in K-feldspar and aggregates of rutile (0.6%) after biotite. There are 1-mm anhedral chalcopyrite grains (3%) disseminated throughout the sample, with chalcocite (0.5%) in fractures in the chalcopyrite. Hypogene mineralization shows quartz-pyrite-chalcopyrite-bornite veins cutting mineral grains. A few grains of pyrite are present. A trace of covellite was seen replacing chalcopyrite. Quartz-molybdenite veins where molybdenite is deposited along both vein walls cut mineral grains. Hypogene alteration displays plagioclase altered to sericite, and biotite altered to rutile and traces of calcite and chlorite. Supergene enrichment is manifest as chalcocite and covellite replacing chalcopyrite. Sericite is altered to kaolinite and yellow-brown staining of sericite by iron oxides is observed.

There appear to be two types of kaolinite present. One type is found within veinlets that cut silicates and sulfides; this kaolinite is stained yellow. This kaolinite does not show the ravages of alteration. The second type of kaolinite appears in feldspar phenocrysts, and looks dirty, not as well crystallized, and looks quite altered. The kaolinite in veinlets appears to be more coarse-grained than the kaolinite in the feldspar phenocrysts.
Drill Hole A-491

Oxide-Leach zone, Sample DH A-491: 1821

The sample is Monzonite Porphyry with 0.15-mm sericite (75%) that replaces plagioclase phenocrysts and 0.3-mm coarse sericite (7%) that replaces biotite phenocrysts, together in a matrix of 0.1-mm quartz (8%). There are veinlets of granular 0.3-mm quartz (6%) and kaolinite (1%) along with hematite (0.5%) and jarosite (0.5%). Minute leucoxene (1%) is present in biotite. No hypogene sulfide mineralization is noted. Hypogene alteration altered all plagioclase to sericite and biotite altered to leucoxene. Multiple generations of veinlets are noted, with a quartz-sericite-kaolinite vein cut by quartz-kaolinite veins. Biotite is altered to sericite and there are void spaces where biotite phenocrysts once resided. A trace of clay is present.

In Figure 2.12, vein #1 traverses the entire length of the section and is comprised of kaolinite and sericite. Vein #2 contains orange-brown iron oxide and is filled with mostly kaolinite with some quartz. The vein is free of sericite. Vein #3 contains mostly quartz with a little kaolinite. Vein A contains mostly quartz with some kaolinite.
Figure 2.12 DH A-491: 1821
No Sulfides Present
Enrichment zone, Sample DH A-491: 1507

This sample is Quartz Monzonite Porphyry with 0.25-mm quartz (20%) in the matrix, 0.15-mm sericite (48%) that replaces plagioclase phenocrysts, and 0.2-mm sericite (7%) that replaces biotite phenocrysts. Veinlets contain granular quartz (20%) and kaolinite (1%). Anhedral 1-mm pyrite (3%) is both disseminated and in veinlets, and trace anhedral 0.1-mm chalcopyrite is disseminated throughout the sample. Anhedral 0.1-mm chalcocite (0.1%) and covellite (0.1%) replace chalcopyrite. Hypogene mineralization exhibits quartz-pyrite-chalcopyrite and quartz-molybdenite veins cutting the monzonite porphyry. There are multiple veins in which the sulfides appear as open space fillings. Hypogene alteration consists of plagioclase altered to sericite, and a sericite alteration halo surrounding a pyrite vein. There is sericite present in the sulfide veins. Supergene enrichment is manifested as chalcocite and covellite replacing chalcopyrite. Biotite is altered to rutile and leucoxene, and biotite is altered to coarse sericite. Sericite in the feldspar phenocrysts alters to clay.
Protore zone, Sample DH A-491: 1380

Sample 1380 is Quartz Monzonite Porphyry with anhedral 1-mm quartz phenocrysts (1%), subhedral 1-mm plagioclase phenocrysts (2%), subhedral 1-mm K-feldspar phenocrysts (6%), and subhedral 0.7-mm biotite phenocrysts altered to muscovite (2%). There is 0.25-mm quartz in the matrix (35%), and 0.2-mm anhedral quartz in veinlets (5.5%). Plagioclase phenocrysts retain their original shape even after having been replaced with 0.7-mm sericite (25.5%). Kaolinite (23%) replaces plagioclase and K-feldspar. Hypogene mineralization exhibits quartz-pyrite-chalcopyrite and quartz-molybdenite veins cutting the monzonite porphyry. Hypogene alteration displays sericite alteration haloes surrounding the quartz-sulfide veins, and plagioclase phenocrysts have been altered to sericite. No secondary enrichment is seen. Sericite in the former plagioclase phenocrysts is altered to kaolinite, and biotite is altered to muscovite.

Almost all the sulfides are in veins and veinlets.
Figure 2.14 DH A-491: 1380
Drill Hole WC-31

Oxide-Leach zone, Sample DH WC-31: 1695-1698

The sample is Precambrian Granite with 2-3-mm anhedral quartz (42%), 2-5-mm anhedral to subhedral K-feldspar (39%), and 0.5-mm sericite that replaces K-feldspar (2%) and all plagioclase (13%). Anhedral 0.5-mm biotite is altered to muscovite (0.3%). Anhedral aggregates of 0.05-mm rutile (0.25%) are found adjacent to altered biotite along with trace amounts of euhedral to subhedral 0.2-mm zircon. Kaolinite (3%) and minute hematite specks (0.7%) are found in K-feldspar. Hypogene mineralization appears as very fine-grains of disseminated pyrite, and as a few grains of disseminated chalcopyrite. Hypogene alteration exhibits plagioclase altered to fine-grained sericite and biotite altered to rutile. Supergene enrichment displays covellite rims on chalcopyrite. Sericite in the former plagioclase phenocrysts is altered to kaolinite, biotite is altered to muscovite, and iron oxide rims surround the pyrite grains as well as stain the kaolinite an orangish color.
Figure 2.15 DH WC-31: 1695-1698
Enrichment zone, Sample DH WC-31: 1353-1356

This sample is Precambrian Granite with 2-3-mm anhedral quartz (67%), 0.15-mm sericite (25.5%) replacing plagioclase, 0.2-mm anhedral unaltered K-feldspar (3%), and a trace of 0.5-mm biotite altered to muscovite. Anhedral 0.5-1-mm pyrite (3%) and anhedral 0.5-mm chalcopyrite grains (0.5%) are in veinlets. A trace of covellite is present along fractures in chalcopyrite. Hypogene mineralization consists of pyrite and chalcopyrite veins as well as quartz-molybdenite veins with molybdenite deposited along both vein walls. Hypogene alteration displays plagioclase altered to sericite. Supergene enrichment appears as covellite rims on chalcopyrite, and a few of the pyrite grains show signs of secondary enrichment with chalcocite. Biotite is altered to muscovite, and sericite in the former plagioclase grains is altered to kaolinite.

In Figure 2.16, the large vein is filled with coarse, euhedral quartz clasts that are in a clay matrix. No sericite is seen.
Figure 2.16 DH WC-31: 1353-1356

Qtz Vein
Protore zone, sample DH WC-31: 1143-1146

Sample 1143-1146 is Precambrian Granite with 1-2-mm anhedral quartz (34.5%), 0.5-1.2-mm anhedral microperthite (29.5%), 0.1-0.5-mm anhedral orthoclase (18%), 0.1-mm plagioclase in microperthite (15%), and traces of 0.1-mm biotite. There are anhedral aggregates of hematite (1%) adjacent to the sulfides. Hypogene alteration displays finely-matted sericite (0.5%) replacing much of the plagioclase. Hypogene mineralization appears as anhedral disseminated chalcopyrite and pyrite. Magnetite is disseminated throughout the sample, and sulfides are clustered around biotite grains. Supergene enrichment appears as chalcocite and covellite rims on chalcopyrite and pyrite. Sericite is altered to kaolinite. Quartz-kaolinite veins cut all other components of the sample.
Figure 2.17 DH WC-31: 1143-1146
CHAPTER 3

MINERALOGIC STUDIES

The objective here is to identify the several phyllosilicate minerals that are present as alteration products. X-ray diffraction from the principal crystallographic planes of phyllosilicates gives unique patterns. The patterns permit determination of the minerals present in a mixture. Phyllosilicate identification was performed by the author at two scales: 1) on aggregate samples of drill core 3 to 4 cm in length using powder mount X-ray diffractometry, and 2) on individual phenocrysts with Debye-Scherrer spindle camera needles to identify alteration products sent for stable isotope analysis.

Selection of Samples

Samples were selected from the same pieces of drill core as thin sections to relate the X-ray data directly to what was observed in petrographic analysis.

X-ray Diffraction Analysis

Phyllosilicates are platy parallel to (001) and will settle from a slurry in preferred orientation with (001) parallel to a glass slide. A preferred orientation slide of each sample was prepared using the following procedure. Samples were crushed to 0.5 to 1 cm with a rock hammer. Fine disaggregation was accomplished by placing the crushed sample in a shatterbox and milling for 8 to 10 seconds to produce a fine powder used in
the sedimentation laboratory. To prevent contamination, clean dry silica was milled through the shatterbox between samples of study material.

Particle sizes of less than 2 microns were separated by combining 10.00 gm of the powdered sample with 1.60 gm of sodium hexametaphosphate \((\text{NaPO}_3)_6\) to prevent flocculation. The mixture was added to a stainless steel blender cup containing 400 ml of deionized water following the procedure of Schreiber (1992a) and agitated for 5 minutes using a commercial Hamilton Beach blender. This mixture was added to 400 ml of deionized water in a clean one-quart Mason jar to give a total volume of 800 ml. The jar was covered and the mixture was allowed to settle at a room temperature of 25° C. According to Stoke's Law, particles greater than 2 microns in water at 25° C will settle through a depth of 5 centimeters in 3 hours and 38 minutes (Schreiber, 1992b). At the end of the settling time, the top 5 centimeters of liquid were removed using a syringe; 45 ml of this liquid was placed into each of two 50 ml centrifuge tubes. The liquid was centrifuged for 10 minutes at approximately 1880 rpm using a model CL International Clinic Centrifuge. The supernatant liquid in the centrifuge tubes was decanted and discarded. Using a clean dry pipette, slurry at the bottom of the centrifuge tubes was transferred to a clean dry Pyrex™ 2.5 x 2.5 cm glass slide and allowed to dry overnight at room temperature.
Diffractometry Procedure

Diffractometry entailed scanning the oriented sample using a Siemens D-500 X-ray diffractometer with Cu radiation (\( \lambda = 1.54178 \, \text{Å} \)) at 40 kV and 30 mA at a scan rate of 2°2\( \Theta \) per minute from 3° to 70°2\( \Theta \) using a count rate of 1 x 10^3 counts per second. The resultant peaks were plotted on a Siemens Kompensograph X–T chart recorder at a recording speed of 2 cm per minute.

Diffractometric Identification of Minerals

Peaks were measured using the 2\( \Theta \) degrees spacing on the chart paper. The 2\( \Theta \) degree values were converted into d-spacings in Angstrom (Å) units using Bragg’s equation \( n\lambda = 2dsin\Theta \) with Microsoft Excel on a Macintosh™ computer. The author used Brown & Brindley (1980) and Chen Pei–Yuan (1977) to help identify the minerals present.

Silica used to clean the shatterbox between samples was identified as pure quartz, so no phyllosilicate contamination occurred between samples. Phyllosilicates that were identified are kaolinite that is characterized with well-defined (001) and (002) intense reflections that are consistent with well-ordered kaolinite. Montmorillonite and 2\( M_1 \) sericite were also identified. No chlorite was identified in any of the samples and no reflections remained unidentifiable. Slides found to contain montmorillonite were placed on a rack in a sealed glass container with ethylene glycol and heated at 60°C for one hour as described by Carroll (1970). The glycolated samples were scanned again using the same settings as had previously been used; swelling of the d-spacings from 12Å to 16-17Å had occurred along with a rational sequence of
higher orders of reflections, indicating the presence of montmorillonite. There were no peaks found in the 14Å range of the glycolated samples, reinforcing the earlier statement of no chlorite being present.

Measurement of basal peak heights were made using the peak-half-height method of Moore and Reynolds (1989 p. 304) and are plotted in Figures 3.1 through 3.5. Although this is not a precise quantitative method of comparison and suffers from problems such as variable grain size, different degrees of crystallinity, and differing mass absorption coefficients, it does allow a basis for observing general trends and has been used on phyllosilicates by Carroll and Hathaway (1963) and by Marozas (1982).

**Sample Preparation**

Fourteen of the 49 drill core samples were chosen for stable isotope analysis. Based upon petrographic analysis of thin sections, samples were obtained from drill core by hand using a steel sewing needle held in a pin vise to remove alteration products from individual feldspar phenocryst sites. Material extracted was placed into labelled gelatin capsules. Once a sufficient amount of material was harvested, it was inspected under a binocular microscope and non-phyllosilicate material was removed by hand using a steel needle.
Figure 3.1

Integrated Intensities of Sericite, Kaolinite, and Montmorillonite in DH 1132

- **Oxide Leach Zone**
  - 1526-1529: Sericite, Kaolinite
  - 1483-1485: Sericite
  - 1400-1403: Sericite
  - 1362-1365: Sericite
  - 1318-1321: Sericite

- **Enrichment Zone**
  - 1280-1282: Sericite, Kaolinite
  - 1258-1260: Sericite, Kaolinite
  - 1237: Sericite

- **Protore Zone**
  - 1161: Sericite, Kaolinite
  - 1159: Kaolinite

Square millimeters under XRD peaks
Figure 3.2
Integrated Intensities of Sericite, Kaolinite, and Montmorillonite in DH 1130

Square millimeters under XRD peaks
Figure 3.3
Integrated Intensities of Sericite, Kaolinite, and Montmorillonite in DH 1193
Figure 3.4

Integrated Intensities of Sericite, Kaolinite, and Montmorillonite in DH A-491

Oxide Leach Zone

Enrichment Zone

Protore Zone

Square millimeters under XRD peaks
Figure 3.6
Integrated Intensities of Sericite, Kaolinite, and Montmorillonite in DH WC-31

Square millimeters under XRD peaks

Oxide Leach Zone

1695-1698
Kaolinite
Sericite
Montmorillonite

1652-1655
Kaolinite
Sericite
Montmorillonite

1603-1606
Kaolinite
Sericite

1536-1539
Kaolinite
Sericite

Enrichment Zone

1445-1448
Sericite

1353-1356
Sericite
Kaolinite

1298-1301
Sericite
Kaolinite

Protore Zone

1158-1161
Sericite
Kaolinite

1155-1158
Sericite
Kaolinite

1143-1146
Sericite

1662-1665
Kaolinite

1603-1606
Kaolinite

1536-1539
Kaolinite

1445-1448
Kaolinite

1353-1356
Kaolinite

1298-1301
Kaolinite

1158-1161
Kaolinite

1155-1158
Kaolinite

1143-1146
Kaolinite
Debye-Scherrer Identification of Clay Minerals

X-ray powder pattern film photos were made of 14 samples using two 114.59 mm Debye-Scherrer cameras with a Phillips diffraction unit using a technique similar to that described by Zadina (1982). A few micrograms of mineral material was taken for each sample, placed on a clean Pyrex™ glass plate, and gently crushed by rolling with a stainless steel dental probe. The resultant powder was scraped into a pile using a stainless steel single-edged razor blade. A 0.5-mm-diameter glass spindle was dipped into slow-drying cement and then rolled in the sample, coating the spindle. The spindle was placed and centered in a camera that was then loaded with Kodak direct exposure DEF-392 Scientific Imaging Film. Exposure times were 3 hours using 40 kV and 25 mA with radiation type CuKα. Lines on the developed films were measured using a metric scale and d-spacings, in angstroms, were obtained by Bragg's equation using Microsoft Excel on a Macintosh™ computer.

Relative abundances of the minerals were determined by the author from the number and intensity of lines of each respective mineral. A system of abundant ++, common +, some Δ, rare −, and trace −− was adopted. The results of the powder camera study are listed in Table 3.1.
Table 3.1
Mineralogy of Stable Isotope Samples

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<th>DH 1193</th>
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Abundances of mineralogy are: abundant ++, common +, some Δ, rare −, and trace −−.
Discussion

Observations from the optical microscopic work showed clay formation occurred at two scales. There is a small-scale replacement of almost all original rock forming plagioclase by clay that was replaced by sericite while K-feldspar was unaffected. At a larger scale and occurring later, there is an almost total replacement of all feldspar and sericite with clay. Schwartz (1947) stated that sodium and calcium silicates are unstable and surrender sodium and calcium to solution whereas potassium aluminum silicates are relatively stable with respect to hydrothermal solutions. Supergene alteration is a process of acid sulfate leaching of alkali cations at a low pH with large volumes of water that is not likely to produce montmorillonite from rocks from which most of the Na, Ca, and Mg have been extracted. Extensive leaching of these cations by low pH fluids favors the formation of kaolinite. When the removal of alkali and alkaline earth cations is not complete, intermediate argillic phases such as montmorillonite occur. This reasoning leads to the conclusion that most of the montmorillonite is of hypogene origin.
CHAPTER 4
WHOLE ROCK GEOCHEMISTRY

An instructive comparison between fresh rock and altered rock is one that quantitatively shows which elements have been added to or subtracted from a known volume of fresh rock due to hydrothermal or supergene alteration. This information is used in conjunction with petrographic and X-ray mineralogic analysis to describe geochemical gains and losses due to hydrothermal and supergene alteration.

Geochemical Gains and Losses

Whole-rock samples were sent to Skyline Laboratories in Tucson, Arizona, for whole rock major element geochemical analysis by X-ray fluorescence, and for trace elements Cu, S, Rb, Sr, Zr, H$_2$O$^-$, and H$_2$O$^+$ and specific gravity determination. The geochemical data is in Table 4.1. Samples plotted at 0.00 reflect values that are below the analytical detection limits.

Samples from the same pieces of core as the thin section and X-ray data were selected to avoid obvious relative sulfide enrichment and as representative samples of the respective intervals. Alteration at Morenci is such that there are no unaltered rocks to serve as end members. The author has chosen a “least-altered granite equivalent” as DH WC-31 1143-1146 from Western Copper, a “least-altered granite porphyry equivalent” as DH 1132 1159 from Northwest Extension, and a “least-altered monzonite porphyry equivalent” as DH A-491 1380 from Metcalf. Gains and losses were calculated using Microsoft Excel on a Macintosh™ computer by recalculating
the values obtained to 100 percent, then multiplying by the specific gravity of the sample to convert units of the analysis into mass per unit volume. The resultant data are subtracted from the selected "least-altered" end-members to give a gain or loss with respect to that end member. The horizontal line in Figures 4.1 to 4.5 represents the unaltered rock composition; gains are plotted above the horizontal line, losses are plotted below it.
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Figure 4.1
DH 1132 Gains & Losses

1526-1529 Oxide-Leach Precambrian Granite
1258-1260 Enrichment Zone Older Granite Porphyry
Figure 4.2
DH 1130 Gains & Losses

![Graph showing gains and losses in various elements in different zones.]

- **1470 Oxide-Leach Older Granite**
- **1200 Enrichment Zone Older Porphyry**
- **1097 Protore Zone Older Granite Porphyry**
Figure 4.3
Gains and Losses Drill Hole 1193

1339-1342 Oxide-Leach Monzonite
1102-1103 Enrichment Zone Quartz
899-900 Protore Zone Precambrian Monzonite Porphyry
Granite
Figure 4.4
DH A-491 Gains & Losses

- 1821 Oxide-Leach Monzonite Porphyry
- 1507 Enrichment Zone Quartz Monzonite Porphyry
Figure 4.5  
DH WC-31 Gains & Losses 

1695-1698 Oxide-Leach Precambrian Granite  
1353-1356 Enrichment Zone Precambrian Granite
Comparison Summary of Petrographic and Geochemical Data

Drill Hole 1132

Protore sample 1159 was used as the "least-altered older granite porphyry equivalent" as an end member for comparison of the oxide-leach and the enrichment zones. The enrichment zone sample 1258-1260 indicates (Figure 4.1) major losses for SiO₂, and minor losses in Al₂O₃, Fe₂O₃, MgO, CaO, K₂O, MnO, P₂O₅, and S, and gains in LOI, H₂O⁺, H₂O⁺, and Cu. The oxide-leach sample 1526-1529 shows losses in Al₂O₃, Fe₂O₃, CaO, Na₂O, Cu, and S, and gains in SiO₂, MgO, K₂O, TiO₂, LOI, and H₂O⁺. The whole rock data agree with what was seen in thin section analysis. The gain in Cu in the enrichment zone is due to chalcocite and covellite, whereas losses are due to alteration of biotite, plagioclase, and potassium feldspar. The gains of SiO₂ and K₂O in the oxidized zone are due to quartz added in vugs and to the presence of sericite.

Drill Hole 1130

All samples are older granite porphyry. Sample 1097 of protore shows (Figure 4.2) a major loss in Al₂O₃, and minor losses in MgO, CaO, MnO, TiO₂, P₂O₅, H₂O⁺, Cu, S, and gains in SiO₂, Fe₂O₃, K₂O, H₂O⁺. The gains in Fe₂O₃ and K₂O correspond to the presence of pyrite and abundant sericite. Sample 1200 of the enrichment zone shows a major loss in Al₂O₃, and minor losses in MgO, CaO, MnO, TiO₂, and H₂O⁺, and a major gain in SiO₂, and minor gains in Fe₂O₃, K₂O, P₂O₅, H₂O⁺, Cu, and S. The gain in Cu corresponds to the presence of chalcocite and covellite, the gain in K₂O
correlates with the abundant sericite, and the gain in Fe₂O₃ is indicated by original pyrite. The loss in Al₂O₃ corresponds with the wholesale alteration of all feldspar, and the loss in MgO is due to the alteration of biotite. The oxide sample 1470 shows a major loss in Al₂O₃, and minor losses in SiO₂, MgO, MnO, TiO₂, H₂O⁺, and S, and gains in Fe₂O₃, K₂O, H₂O^+, and Cu. The gain in Cu is attributable to the presence of chrysocolla. The gain in Fe₂O₃ is due to iron oxides after pyrite. The increase in K₂O is due to the abundance of sericite. The loss in Al₂O₃ corresponds to the complete destruction of all the feldspar.

Drill Hole 1193

This hole has no oxide-leach zone, the enrichment zone continuing all the way to the top of the hole. Sample 899-900 (Figure 4.3) from protore shows a major loss in Al₂O₃, and minor losses in MgO, H₂O⁺, H₂O⁻, and S, and a major gain in Fe₂O₃, and minor gains in SiO₂, K₂O, and Na₂O. Gains in Fe₂O₃, K₂O, are shown by pyrite and iron oxides, and the presence of sericite. The loss in Al₂O₃ would correspond with the alteration of the feldspars. The two samples 1102-1103, and 1339-1342 show almost total agreement in gains and losses of both major and trace elements. Both showed major losses in SiO₂, and Na₂O, and minor losses in H₂O⁺, and H₂O⁻, a major gain in Al₂O₃, and a minor gain in TiO₂. The two differ in that the sample from 1102-1103 meters shows a loss in S and gains in MgO and CaO, whereas the sample from 1339-1342 meters shows gains in Fe₂O₃, Cu, and S. The whole rock data corresponds with thin section analysis indicating the presence of chalcopyrite, chalcocite, and covellite.
Drill Hole A-491

Both samples are Monzonite Porphyry. The oxidized zone sample 1821 (Figure 4.4) indicates minor losses in MgO, CaO, Na₂O, K₂O, H₂O⁺, H₂O⁻, Cu, and S and minor gains in SiO₂, Fe₂O₃, and TiO₂. The enrichment zone sample 1507 indicates minor losses in MgO, CaO, Na₂O, K₂O, P₂O₅, and H₂O⁺, major gains in SiO₂ and Fe₂O₃, and minor gains in Al₂O₃, Cu, and S. Sample 1380 from protore is the "least-altered Monzonite Porphyry equivalent". The whole rock data agree with what was noted on thin section analysis. Increases in Fe₂O₃, Cu, and S in the enrichment zone coincide with the presence of chalcocite and sericite. Losses of SiO₂, CaO, Na₂O, MgO and Al₂O₃ can be explained by the alteration of plagioclase, K-feldspar, and biotite. The loss in K₂O is explained by there not being any K-feldspar in samples 1821 and 1507, yet K-feldspar is present in sample 1380.

Drill Hole WC-31

Sample 1143-1146 (Figure 4.5) from the bottom of this hole is used as the "least-altered Precambrian Granite equivalent" as an end member for comparison of the oxide and enrichment zones. Figure 4.5 shows a major gain in SiO₂, minor gains in MgO, and K₂O, a major loss of Na₂O, and a minor loss in CaO for both zones. Sample 1353-1356 from the enrichment zone shows gains in Al₂O₃, Cu, and S and losses for Fe₂O₃, and LOI. Sample 1695-1698 from the leach-oxide zone shows gains of Fe₂O₃, MgO, TiO₂, and LOI, and losses for Al₂O₃, H₂O⁺, Cu, and S. The gains and losses data agree with what was noted in thin section analysis. The large increase in SiO₂ is due to addition of secondary fine-grained quartz in the matrix.
CHAPTER 5

STABLE ISOTOPE STUDIES

Analysis of $^{18}O/^{16}O$ and D/H ratios (where D is deuterium $^2H^+$, the heavy isotope of hydrogen) in phyllosilicate alteration assemblages can determine the provenance of waters involved with alteration-related ore deposition. The isotopic compositions of oxygen and hydrogen of a sample are expressed as per mil differences relative to SMOW or Standard Mean Ocean Water using the following equations:

$$\delta^{18}O = \left( \frac{^{18}O/^{16}O_{\text{sample}} - ^{18}O/^{16}O_{\text{SMOW}}}{^{18}O/^{16}O_{\text{SMOW}}} \right) \times 1000$$

$$\delta D = \left( \frac{D/H_{\text{sample}} - D/H_{\text{SMOW}}}{D/H_{\text{SMOW}}} \right) \times 1000$$

Positive values of $\delta^{18}O$ and $\delta D$ indicate enrichment of the sample with $^{18}O$ and D compared to SMOW and negative values imply depletion of $^{18}O$ and D in the samples relative to SMOW (Faure, 1986). Hydrogen and oxygen stable isotope values of SMOW, are thought to have remained constant since Precambrian time (Sheppard, 1977).

Magmatic Solutions

Water in felsic magmas varies from 2.5 to 6.5 weight percent (Pirajno, 1992); it exsolves out of crystallizing magmas at 500° to 1100° C. Magmatic waters typically have uniform $\delta^{18}O$ values of +5.5 to +9.5 and $\delta D$ values of −40 to −80 worldwide (Sheppard, 1977). Crystallization of a felsic magma causes water vapor pressure to increase at the top of the intrusion to a point
where the internal pressure of the water is equal to lithostatic pressure, beyond which a separate aqueous solution forms (Sheppard, 1977; Pirajno, 1992). Hydraulic fracturing of the solidified outer shell of the magma occurs when the pressure of the aqueous solution is greater than lithostatic pressure and the tensile strength of the rock (Henley and McNabb, 1978). This release in pressure causes more water-saturated melt to crystallize, which releases more aqueous solution. Multiple fracturing of the solidified shell creates channels for mineralizing solutions and heat to be transported from the magma upward. Introduction of a hot aqueous magmatic hydrothermal solution out of equilibrium with the surrounding rock generally initiates alkalic, particularly potassic, metasomatism.

**Meteoric Solutions**

Meteoric water is rain and snow precipitation from clouds onto the crust of the Earth. Meteoric waters exhibit geological and geographical stable isotope distributions that derive from the effects of meteorological processes on mass differences between isotopes. Hydrogen and oxygen isotope fractionation is governed by the processes of evaporation and condensation (Taylor, 1974; Faure, 1986). Atmospheric water vapor is isotopically lighter than the oceans from which it evaporated. Precipitation is isotopically heavier than the remaining water vapor within the clouds. As clouds move across the continents, land closest to the ocean will receive precipitation that is isotopically heavier than land further inland since each successive precipitation is isotopically lighter. Higher elevations and latitudes receive precipitation lower in values of $\delta D$ and $\delta^{18}O$ due to temperature dependent
fractionation. Waters that are the most depleted in D and $^{18}$O are in the polar regions (Taylor, 1974). This systematic isotopic variation of meteoric water allows one to plot all meteoric water by the equation (Taylor 1974):

$$\delta D = 8d^{18}O + 10 \text{ (per mil)}$$

and is shown as the meteoric water line in Figure 5.1.

Magmatic-Meteoric Model for Porphyry Copper Deposits

Taylor (1974) describes a two-fluid model that characterizes the different alteration types present in a porphyry copper deposit. Based on stable isotopes of oxygen and hydrogen, Taylor (1974) suggested that early hydrothermal alteration was due to magmatic water that occurred in the apical portion of a crystallizing magma; the second fluid was meteoric groundwater. Emplacement of magma fractures the country rock and initiates convective motion of meteoric groundwater through it (Norton, 1982). Additional fractures are caused by thermal expansion of pore fluids due to heating by the adjacent intrusion. Heidrick and Titley (1982) indicate that early fractures can occur at significant distances from the cooling intrusive, but that fracturing events retreat back toward the intrusion with time. Groundwater nearest the intrusion is heated, becomes less dense, and is displaced upwards to be supplanted by cooler, denser fluids farther away. The size of the external hydrothermal system is dependent upon the availability of groundwater and permeability of the country rock. The amount of thermal energy contained within a magma is finite, and as time passes, temperatures decrease due to cooling. After the magma has solidified,
generation of magmatic fluids ceases, but the external convective cell continues to convect, allowing the external hydrothermal system to "collapse" in upon the hydrothermally altered rocks of the inner system (Taylor, 1974; Gustafson and Hunt, 1975). This "collapse" is thought to remobilize existing chalcopryrite (Brimhall, 1980), initiate argillic and phyllic alteration which overprints hypogene potassic and propylitic alteration, and causes sulfide deposition at the interface of the potassic/phyllic boundary forming an ore shell (Lowell and Guilbert, 1970).

Use of Stable Isotopes

The kaolinite line in Figure 5.1 defines the isotopic variations of kaolinites formed in surface weathering environments and can be described by the equation (Faure, 1986):

$$\delta D = 7.5 \delta^{18}O - 220 \text{ (per mil).}$$

Supergene minerals form in equilibrium with meteoric waters at temperatures from 50° to 60° C as a result of pyrite oxidation (Taylor, 1974) and plot to the left of the kaolinite line. Hypogene alteration phyllosilicates form in equilibrium with waters at 200° to 300° C and plot closer to the meteoric water line (Figure 5.1). The reason for this is that at elevated temperatures phyllosilicates that equilibrated isotopes with a fluid have $\delta^{18}O$ and $\delta D$ values that approach those of the fluid because the fractionation factors approach unity with increasing temperatures (Faure, 1986).
The "magmatic waters" box represents probable isotopic composition of hydrothermal fluids generated by magmatic processes, and having a composition in equilibrium with igneous minerals (Beane, 1982).

**Preparation Techniques**

Samples obtained from drill core were sent to Geochron Laboratories in Cambridge, Massachusetts, for oxygen isotope analysis and both oxygen and hydrogen analysis on a biotite sample. Hydrogen/Deuterium analyses were done by the author in the Stable Isotope Laboratory in the Department of Geosciences at the University of Arizona.

Determination of D/H ratios was performed on $\text{H}_2$ gas. Approximately 25 mg of sample material was placed in a silica glass tube and heated in a platinum resistance furnace at 1000° C for 10 minutes. Water vapor carrying most of the hydrogen given off by hydrous minerals was then passed over a uranium furnace at 750° C (Hoefs, 1987). The resulting hydrogen gas was collected in glass ampules labelled with the drill hole and elevation and taken immediately to the mass spectrometer. A Finnigan MAT delta S mass spectrometer running ISODAT software was used to analyze the D/H ratio of the hydrogen gas. Hydrogen standard lab gas was first analyzed to obtain a zero reading. Each ampule of hydrogen gas was fitted to the mass spectrometer, which ran 2 separate analyses from each ampule and calculated a D/H ratio relative to SMOW for each analysis.
Hydrogen and oxygen isotope data are shown in Table 5.1 and are plotted in Figure 5.1, along with lines representing magmatic water, meteoric water and kaolinite clays. Also shown is data from an igneous biotite sample deep within the protore of the Morenci pit obtained with assistance of Rick Preece, and a Morenci clay sample from Sheppard, Nielsen, and Taylor (1969).

In Figure 5.1 one notices 3 groups of data. Biotite falls within the magmatic water box indicating that biotite formed in equilibrium with fluids generated by magmatic processes at magmatic temperatures. A second group of data points near the magmatic water box are sericite from oxide-leach, enriched, and protore zones with $^{18}$O values close to those of hypogene magmatic waters which is consistent with a low meteoric water to rock ratio during the development of the sericite (Sheppard, 1977). The other data points are two populations of apparently supergene kaolinite that show a wider variation in the $^{18}$O values of the kaolinite which suggests a greater meteoric water presence. Kaolinite that plots in between the sericite and the kaolinite near the kaolinite line is first cycle enrichment. Kaolinite that plots to the immediate left of the kaolinite line is second-generation enrichment at lower temperatures, with the lowest data point being in equilibrium with present-day meteoric water as it falls very near to the kaolinite line.
Data in Figure 5.1 shows sericite in oxide-leach capping plotting in hypogene space; this may be due to a combination of the following:

1. Hypogene sericite may or may not be in chemical equilibrium with supergene fluids, but it is not in isotopic equilibrium with them.

2. The kinetics of reactions that alter sericite to kaolinite are so slow that no change is seen since the onset of supergene alteration.

Figure 5.1 also shows protore plotting in supergene space and may be the result of high permeabilities due to abundant fractures that allow meteoric water to access deep portions of the deposit.
Table 5.1
Stable Isotope Data

<table>
<thead>
<tr>
<th>Reference</th>
<th>Drill Hole WC-31</th>
<th>Drill Hole A-491</th>
<th>Drill Hole 1132</th>
<th>Drill Hole 1193</th>
<th>Drill Hole 1130</th>
<th>Drill Hole MO-1</th>
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<tbody>
<tr>
<td>Number</td>
<td>Elevation (meters)</td>
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<td>ΔD</td>
<td>Zone</td>
<td>Mineralogy</td>
<td>ΔO18</td>
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<tr>
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<tr>
<td></td>
<td>* Denotes sample from a kaolinite vein</td>
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<td></td>
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</tbody>
</table>

Sheppard, Nielsen, and Taylor 1969
Figure 5.1
Plot of Stable Isotope Data
Numbers Refer to Sample Descriptions in Table 5.1

- Magmatic Waters
- Meteoric Water
- Kaolinite Line

δD (‰) SMOW

δ18O (‰) SMOW

- Sericite in Oxide-Leach
- Kaolinite in Protore
- Biotite
- SNT(1969) Morenci Kaolinite
- Sericite in Enrichment
- Sericite in Protore
- Kaolinite in Oxide-Leach
- Kaolinite in Enrichment
CHAPTER 6

DISCUSSION AND CONCLUSION

There is no unaltered rock at Morenci. An almost total destruction of the monzonite and granite porphyries evidenced in petrographic and geochemical study is consistent with meteoric water and high rock permeability. In reporting fluid inclusion data, Preece, Stegen, and Weiskopf (1993) state that the early sulfide-deficient veins were a result of water-rock reactions dominated by the wallrocks, and that sulfide deposition was contemporaneous with low-salinity fluids far out of equilibrium with the surrounding rocks in quantities that controlled the water-rock reactions.

Reasons for such extensive supergene alteration at Morenci are: 1) high pyrite to chalcopryrite ratios allow for a greater amount of acid production, and 2) extensive hypogene phyllic alteration that resulted in far fewer reactive minerals to be present along the meteoric supergene solution path resulting in low pH because no buffering of the solutions took place.

Climatic conditions influence the oxidation of sulfide deposits by controlling chemical weathering which is dependent upon temperature and amounts of precipitation (Anderson, 1982). Temperature influences the rate of chemical reactions, such that tropical climates promote rapid chemical reactions, and polar climates prevent significant chemical reactions. Stable isotopes of oxygen and hydrogen from Taylor (1974) indicate that the Eocene climate was abnormally hot. Floral remains from the Eocene indicate a warm, humid climate conducive to rapid regional weathering (Scarborough,
This period of intense weathering and erosion is considered responsible for the production of the mineralized supergene blankets for many of the porphyry copper deposits in the southwestern United States (Scarborough, 1989).

Rapid erosion and leaching of copper that followed emplacement of the Laramide porphyries allowed for a first-generation supergene blanket to form. Moolick and Durek (1966) stated that there was weathering of the deposit prior to Mid-Tertiary magmatism with oxidized copper minerals in contact with basaltic flows. North and Preece (1993) state that the enrichment front appears to have descended at a rate about equal to erosion for much of the period between 56 Ma and the onset of Mid-Tertiary volcanism. Mid-Tertiary volcanism covered the deposit, halted the weathering and erosion and preserved the deposit. Livingston, Mauger, and Damon (1968) give a date of 33 Ma for the Clifton volcanics four miles from Morenci. Basin and Range tectonism in the district uncovered the deposit and initiated a second round of weathering and erosion that gave rise to the second-generation supergene blanket. The important factor of the weathering of the first-generation blanket was the pyrite content of the blanket. Where the pyrite content was high, chalcocite and pyrite were leached leaving behind a hematitic leached cap. Copper was carried downward and redeposited on chalcopyrite and pyrite as a second-generation supergene blanket. Areas of low pyrite content resulted in insufficient acid generation to keep the copper in solution. The copper was oxidized in place and resulted in the formation of chrysocolla, brochantite, azurite, and malachite. Climates of the Miocene became cooler and drier, along with a change in precipitation to a more monsoon-type.
That all samples fall outside the magmatic waters box of Figure 5.1 is evidence to support the idea that meteoric waters played a role in both supergene and hypogene alteration at Morenci. Sheppard, Nielsen, and Taylor (1969; 1971) and Taylor (1974; 1979) concluded that both magmatic and meteoric waters played an important role in the time-staged aspects of development of the Santa Rita porphyry copper deposit. Sheppard, Nielsen, and Taylor (1969) noticed a vertical zonation of alteration minerals at Santa Rita where they identified oxide-leach capping and enrichment samples as supergene and protore as hypogene. Stable isotope data from Morenci does not show the same type of vertical zonation. In fact, the data shows the opposite, with oxide-leach cap samples from the top of drill holes plotting with hypogene samples and protore samples from bottom of the drill holes plotting near the kaolinite line. This data reinforces the idea put forth by Sheppard, Nielsen, and Taylor (1969; 1971) that phyllosilicates do not readily exchange oxygen and hydrogen once they have formed. With a 51 Ma (Forrester, 1997) date obtained from sericite at Morenci, one concludes that sericite has retained its stable isotope signature since its time of formation. Petrographic examination showed kaolinite present in the protore zone as open space filling in veinlets that plots near the kaolinite line in equilibrium with late supergene waters that flow down fractures to be deposited at depth.
Evidence of supergene kaolinite at depths within the protore zone lends support to the idea that the rocks at Morenci have historically had a high permeability. Sericite in the oxidized-leach zone indicates a magmatic signature. A reason for this could be these rocks were at depth within the hypogene zone, but today are near the top of present day drill holes.
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